Highly Efficient Catalysts for the Dimerization of α-Olefins

Dissertation

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To my parents, for their constant support

and

to Ise, for her patience, encouragement and love…

Abbreviations

°C	degree celsius
Å	Ångström
δ	chemical shift (ppm)
BTX	benzene, toluene and xylene aromatics
d	doublet
equiv.	equivalent
Et	ethyl
g	gram
GC	gas chromatograph
h	hours
Hz	Hertz
i	*iso*
J	coupling constant (Hz)
LAO	linear alpha olefin
LLDPE	linear low density polyethylene
m	multiplet
MAO	methylaluminoxane
Me	methyl
min	minute
ml	milliliter
mmol	millimol
NMR	nuclear magnetic resonance
Ph	phenyl
q	quartet
rt	room temperature
s	singlet
SHOP	Shell higher olefin process
thf	tetrahydrofuran
TOF	turn over frequency
TON	turn over number

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1. Zusammenfassung

Ziel dieser Arbeit war die selektive katalytische Dimerisierung von α-Olefinen, insbesondere die Dimerisierung von Propen. Die Optimierung der verschiedenen Zielgrößen und Einflussfaktoren der Katalyse, wie die Steuerung der Selektivität und der Aktivität, Lebensdauer der Katalysatoren und Produkttrennung lag hierbei im Vordergrund.

Frühere Arbeiten in der Arbeitsgruppe haben das Potential von Bis(imino)pyridin-Vanadium(III)-Komplexen als Katalysatoren für die Oligomerisation und Polymerisation von Ethylen nach Aktivierung mit Methylaluminoxan aufgezeigt. Eine Reihe neuer und bereits literaturbekannter Komplexe dieses Typs wurde in dieser Arbeit auf ihre katalytische Aktivität hinsichtlich der Dimerisierung von Propen untersucht. Hierbei konnten hohe Selektivitäten hinsichtlich dimerer Produkte, aber auch innerhalb der Hexenisomere erreicht werden. Die Auswertung der Dimerisierungsreaktionen zeigte den zum Teil immensen Einfluss bestimmter Substitutionsmuster oder Substituenten auf die Produktverteilung. Sterisch anspruchsvolle Gruppen an den ortho-Positionen der Iminophenylringe wirkten sich mit zunehmender Größe positiv auf die Dimerenausbeute aus. Das Additiv Triphenylphosphan hatte wenig Auswirkung auf das Dimer / Oligomer Verhältnis, hingegen großen Einfluss auf die Bildung bestimmter Hexenisomere. Während ohne Additiv fast ausschließlich 2-Methyl-1-penten gebildet wurde, war das Hauptprodukt mit Additiv 4-Methyl-1-penten.

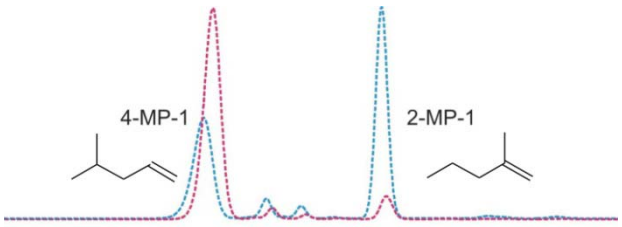


Abbildung 1. Ausschnitt eines GC-Spektrums; Produktbildung mit Additiv (rot) und ohne Additiv (blau).

Aufgrund der mittleren Aktivitäten der Vanadium-Komplexe von 95–215·10^3 g(dimer)/mol h wurde die Optimierung der Aktivität an einem System, welches aus einem Phosphan-Nickel-Chelatkomplex und $EtAlCl_2$ besteht, untersucht. Hierbei wurden bei einer Aktivierung von 1:1000 (Ni:Al) extrem hohe Aktivitäten von bis zu 52·10^6 g(dimer)/mol·h für die katalytische Dimerisierung von Propen beobachtet.

Damit sind solche Katalysatoren vergleichbar mit den aktivsten literaturbekannten Systemen. Die Aktivität blieb nach mehreren Wiederholungen der Katalyse ähnlich hoch und zeigte damit eine erstaunliche Katalysatorlebensdauer. Bei Verwendung von 1-Buten beobachtete man etwas niedrigere katalytische Aktivitäten. Die höchste Selektivität für dimere Produkte (94 % für Propen) wurde bei höherer Aktivierungsrate aber auch wesentlich niedrigeren Aktivitäten erreicht. Nach der Heterogenisierung der Katalysatoren erhöhte sich die Dimerenselektivität auf 100%. Beide Reaktionsbedingungen zeigten die gleiche Produktverteilung innerhalb der Hexenisomere, was sich auf gleiche katalytische Spezies zurückführen lässt. Die Verwendung eines Festbettreaktors veränderte die Verweildauer der Reaktanden am Katalysator, verringerte dadurch die Bildung höherer Oligomere und bestimmte somit die Produktselektivität. Des Weiteren bietet die einfache Produktabtrennung im heterogenen System einen klaren Vorteil gegenüber homogen geführten Reaktionen. Die Vereinfachung der Produkttrennung war die Idee für das Design weiterer Katalysatoren für die Dimerisierung von Olefinen. Dazu wurden Nickel-Komplexe mit Phenoxyimin- oder Bisiminliganden mit funktionellen Gruppen für die nachfolgende kovalente Verknüpfung mit einem Kern-Schale Träger versehen. Dieser mit einer Silica-Hülle funktionalisierte magnetische Eisenkern kann mittels eines magnetischen Feldes aus der Reaktionslösung abgetrennt werden.

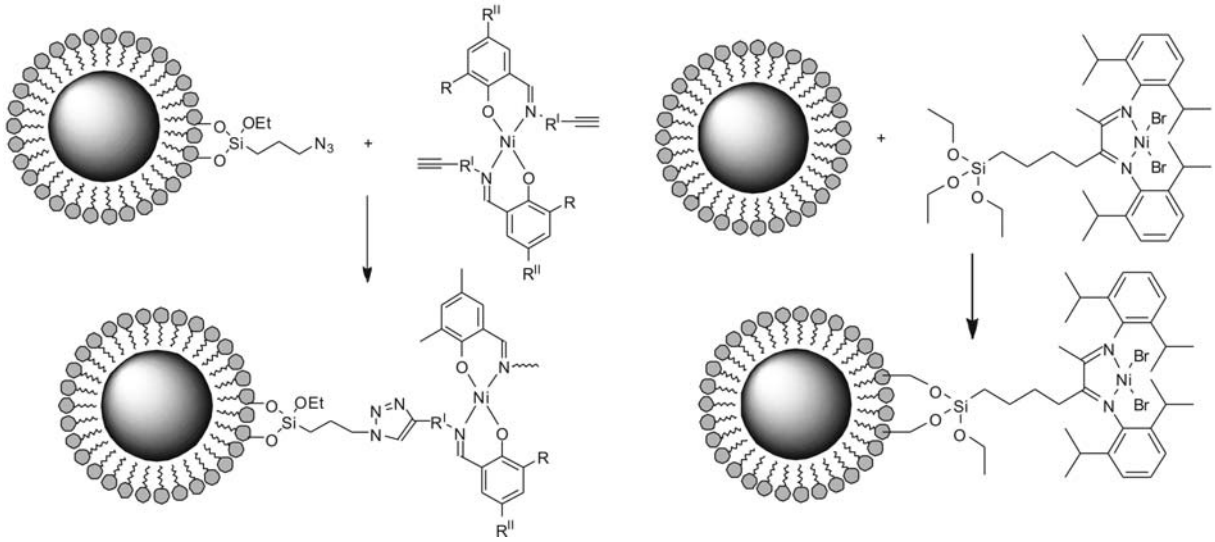


Abbildung 2. Heterogenisierung der Phenoxyimin- (links) und Bisiminnickel Komplexe (rechts).

Die dabei verwendeten Komplexe zeigten nach der Aktivierung mit MAO als „freie“ und als geträgerte Katalysatoren ähnliche hohe Aktivitäten und Produktselektivitäten

für die Dimerisierung von Propen. Auch hier waren unter beiden Bedingungen die gebildeten Produkte gleich. Die dargestellten Komplexe können daher sowohl in der homogenen, als auch in der heterogenen Katalyse verwendet werden und bieten somit Potential für eine Reihe von Anwendungen.

Im letzten Kapitel dieser Arbeit wird ein sehr selektives System für die Dimerisierung der α-Olefine C_3-C_6 sowie *cis*-Buten beschrieben. Die besondere variable Form und Struktur des Liganden erlaubt es, mit einem Zentralmetall verschiedene Koordinationszustände und Koordinationszahlen einzugehen. Salze der frühen und späten Übergangsmetalle Titan, Cobalt und Nickel wurden in verschiedenen Verhältnissen mit dem potentiellen Liganden gemischt und nach Aktivierung mit MAO auf die katalytische Dimerisierung von Olefinen untersucht.

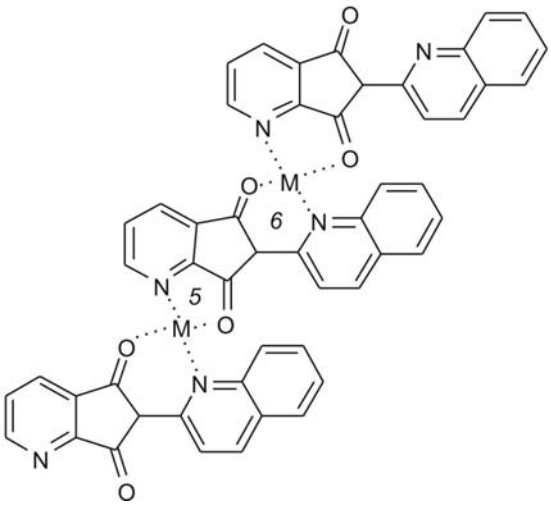


Abbildung 3. Verschiedene Möglichkeiten der Koordinationszustände bei Variation des Ligand / Metall Verhältnisses.

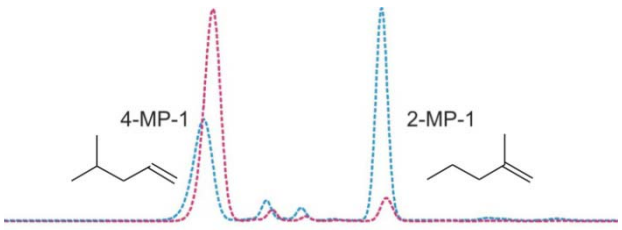
Während bei Verwendung von Nickel-Komplexen die höchsten Aktivitäten für die kurzkettigen Olefine Propen und 1-Buten erreicht wurde, waren die Aktivitäten der Titan-Komplexe für die längeren Olefine 1-Penten und 1-Hexen am höchsten.

Eine Erhöhung des Aktivierungsverhältnisses von 1:500 auf 1:1000 erhöhte die katalytische Aktivität aller Versuche. Komplexe mit dem Zentralmetall Nickel wiesen in allen Versuchen hohe Selektivitäten auf; in einigen Fällen wurde eine 100%ige Selektivität für dimere Produkte erreicht. Titan- und Cobalt-Komplexe erreichten ebenfalls hohe Werte für die Dimerselektivität, welche aber in allen Versuchen niedriger lagen als die mit dem Nickel-System erreichten Werte.

Summary

The aim of my work was the catalytic dimerization of α-olefins, especially the dimerization of propylene. The focus was laid on the optimization of product selectivity, catalyst lifetime, and product separation.

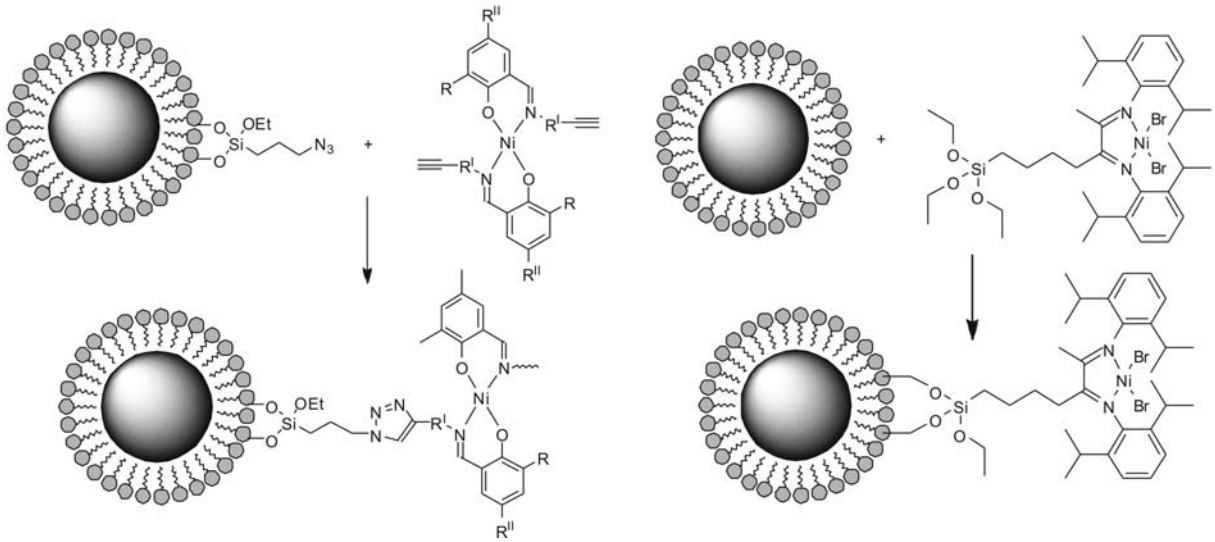
Previous studies in our group have shown the enormous potential of bis(imino)pyridin vanadium(III) complexes as catalysts for the oligomerization and dimerization of ethylene after activation with MAO. A series of new and literature known complexes was synthesized and tested for the homogeneous catalytic dimerization of propylene after activation with MAO. High selectivities towards dimeric products and within the hexene isomers were observed. The evaluation of the dimerization reactions showed a remarkable influence of the substitution pattern at the ligand framework on the product distribution. Steric demanding substituents at the ortho positions of the iminophenyl ring had positive effects on the dimer yield. The influence of triphenylphosphine as an additive was investigated and strong dependencies could be observed. Addition of triphenylphosphine had no effect on the dimer / oligomers ratio but resulted in the formation of mainly 4-methyl-1-pentene instead of 2-methyl-1-pentene (without additive).



Scheme 1. Part of a GC spectra, formed products with (red) and without (blue) the use of additive.

Because of the moderate activities of 95–215 10^3 g(dimer)/mol h of the vanadium catalysts, the optimization of the catalytic activity was studied with a phosphine chelated nickel system in the presence of $EtAlCl_2$. Very high activities of up to $52 \cdot 10^6$ g(dimer)/mol·h were observed with an activation ratio of 1:1000 (Ni:Al). These results are comparable to the most active literature known systems. Applying this activation ratio, catalyst life time experiments were performed. Even after seven repetitions of the dimerization experiments, the catalysts showed high activities of up to 87 % of

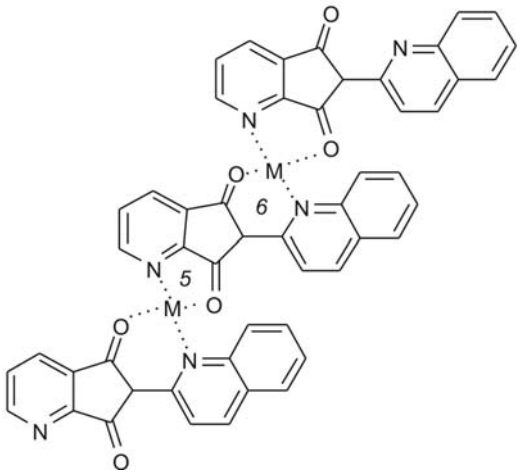
the starting activity. Higher activation ratios resulted in higher selectivities of dimeric products (94 %) but lower activities. After the heterogenization of the catalysts, the amounts of dimeric products were constantly 100%. Under homogeneous and heterogeneous reaction conditions, the same product distributions within the dimer fractions were observed. The use of a fixed bed reactor changed the contact times of the reactants and the catalyst and consequently prevented the formation of higher oligomers and determined the product selectivities. The facile product separation of a heterogeneous system is a great advantage in contrast to the homogeneous system.
The simplification of the product separation was the idea for the design of a series of catalysts for the dimerization of propylene. Nickel complexes with phenoxyimine or bisimine ligands were substituted with functional groups for a subsequent covalent linkage with a core shell support material. This silica functionalized magnetic iron core can be separated from the reaction solution by a strong magnetic field.



Scheme 2. Route of heterogenization of phenoxyimine- (left side) and bisimine (right side) nickel complexes.

The nickel complexes showed comparable high selectivities and activities for the dimerization of propylene after activation with MAO both under “free” and supported conditions in a closed system. Under both settings, the same products were formed. The described complexes can be used in open or closed systems and offer a high potential for a number of applications.
The last chapter of this thesis deals with a very selective system for the dimerization of α-olefins C_3-C_6 and *cis*-butene. The special shape of the ligand allows various

coordination states for the central metal. The early and late transition metals titanium, cobalt and nickel were combined in different ratios with the potential ligand and tested in dimerization reactions after activation with MAO.



Scheme 3. Coordination states; five and six membered rings and possible super lattices.

While nickel complexes provided the highest activities for the short chain olefins propylene and 1-butene, titanium complexes were more active for the higher olefins 1-pentene and 1-hexene. A change of the activation ratio from 1:500 to 1:1000 raised the activities in all cases. Nickel containing complexes showed high selectivities of even 100% for dimeric products. Titanium and cobalt complexes were selective as well, but did not reach the values of the nickel system.

2. Introduction

The chemical industry is the foundation of nearly all parts of modern economy. The securing of base chemicals supply is one of the challenges of the 21th century. A long term view shows that national economies need to be supplied with raw materials and base chemicals in big scales. Sources for this industrial demand can either be fossil deposits (oil, natural gas and coal), regenerative biomass (regrowing raw materials) or carbondioxide / carbonates. The living nature and the main part of the chemical industry are based on carbon containing compounds.[1]

Seen from the chemical side, crude oil is a high complex mixture of hydrocarbons and other organic compounds containing heteroatoms like sulfur, oxygen and nitrogen.

This “Black Gold” is the dominating raw material for the production of organic base chemicals like short chain olefins and aromatic compounds and is the only source for all required base chemicals, especially benzene, toluene and xylene (BTX).[2] In refinering processes crude oil is divided in different fractions depending on the boiling ranges. These fractions are converted, mostly catalytically, in conformed to standards fuels or fuel oil. One of the most common processes for generating feedstocks for base chemicals is the so called steamcracking of light petrols. In this petrochemical method the hydrocarbon feed gets cracked in the presence of water at high temperatures (ca. 850°C). Target products are the light olefin molecules ethylene and propylene. A second important process is the reforming of heavy petrol with platinum containing catalysts, which generates hydrogen and aromatic hydrocarbons (BTX-aromatics).[3] These olefins and aromatics produced via steamcracking and reforming create the crude oil rooted base chemicals of a value creation chain, along which a huge part of organic products get produced. The direct conversion of short alkanes to chemical products and the catalytic conversion of heavy oils (from oil and tar sands) are still challenges for catalytic researches.

Natural gas mainly consists of methane and - differing from the source - amounts of higher alkanes. In single plants in South Africa, Malaysia or Qatar, natural gas gets transformed into high-grade diesel or jet fuel during a three step process.[4] Methane is commonly converted to synthesis gas followed by the Fischer Tropsch process. Up to now, methane plays no role as an educt for base chemicals, except its conversion products hydrogen and synthesis gas. For intercontinental transportation, natural gas has to be liquefied (liquefied natural gas, LNG). Because of these transportation

problems, a direct route from natural gas to higher hydrocarbons or chemical products via catalysis has to be found. The thermodynamic stability and the inertness of methane and short alkanes are challenges for catalytic studies.

Coal was the main raw material source until the mid of the 20th century. Three main procedures exist for the exploitation of fuels and base chemicals out of coal: Gasification (mixtures of synthesis gas), hydrogenation (gaseous and liquid hydrocarbons) and pyrolysis (coke, gaseous and liquid hydrocarbons).[5] Due to its enormous reserves (statistical reach of the current reserves 200 years), coal becomes more and more important for a second time. All organic base chemicals can be manufactured out of the raw material coal; the big issue is the economy and ecology of chemical transformation processes.[1]

Fossil or regenerative carbon sources need to be converted and processed in huge scales. For all sources of raw materials, catalysis seems to be the key technology. Whether the focus is economy, ecology or selectivity, a tailor made catalyst or catalytic system is the focus for industrial processes. More than 80 percent of all globally produced chemicals are synthesized using catalytic processes. In fact, without catalysis, the synthesis of many products in the modern world would be inconceivable.[6]

The first definition of the expression “catalysis” goes back to J. Berzelius in 1836. He used the Greek term “katalysis”, which means as much as “dissolution” and gives a first hint of the basic mechanism of a catalytic reaction.[7] The Chinese ideogram for catalysis “tsoo mei” also describes the term “wedding broker”.[7] The contradiction is merely apparent because, in a chemical reaction, bonds between atoms are broken, but new bonds are also formed. For the breakup and the formation of bonds, energy barriers have to be lowered, which is achieved through the “brokering” by a catalyst. The first modern definition of the term “catalyst” was given by Wilhelm Ostwald in 1895: “A catalyst is a substance which alters the rate of a chemical reaction without itself appearing in the products.”[8] A catalyst takes part in the reaction, but does not appear in the final products and should therefore theoretically not be consumed. It took 50 years after Berzelius definition to develop the first industrial scale process: the synthesis of sulfuric acid applying the contact process.[2] Catalysis itself has an old tradition, starting with the discovery of biocatalysis. Alcoholic fermentation is probably the first (bio)catalytic process that mankind actively made use of. Over 5000 years ago, Egyptians found that yeast converted the sugar in fruit juices to alcohol.

The discovery that the presence of a small amount of a compound has a crucial influence on the conversion of other substances lasted for centuries in the search for the “philosopher`s stone”, which was supposed to convert silver or lead to gold.

Two major types of catalysis can be differentiated:

- Homogeneous catalysis, in which the catalyst, the starting materials and even the formed products are dissolved in the same phase, the reaction medium.
- Heterogeneous catalysis, in which the catalyst is present in a solid state and the reagents are applied in a solid, liquid or gaseous form, therefore innately separating reagents and catalyst into two different phases.

Heterogeneous catalysis has by far the greatest significance in industrial chemistry, given that about 80 percent of all catalytic processes employ a heterogeneous catalyst.[9] The three most important advantages of heterogeneous catalysis are that they can be removed easily from the reaction medium, that the reactors do not corrode and that it is possible to work at relatively high temperatures. This makes this kind of process interesting for chemical industry, mineral oil processing industry and in pollution control.

Unsatured hydrocarbons are versatile relevant intermediates for numerous applications like polymerization, oligomerization and metathesis reactions. The olefinic products can also be used for co-polymerization (C4 – C8), plasticizer (C6 – C10), cleaning agent additives and lubricants (C12 – C16, C30+) and detergent or plasticizer alcohols (C6 – C18).[10] Individual carbon chain lengths handle individual markets with individual challenges. Linear alpha olefins (LAOs) producers may broadly be grouped into two main categories: full range producers and on-purpose producers. The three largest full range producers of LAOs via ethylene oligomerization are Shell, Innovene and Chevron Phillips.[11] These metal catalyzed routes produce a mathematical Schultz-Flory or Poisson distribution of α-olefins, which very often does not match market demands. In particular, around one-half of the LAOs produced are employed as comonomers for the production of linear low-density polyethylene (LLDPE) copolymers, which utilize 1-butene, 1 hexene, and 1-octene fractions.[12] The mechanism of these oligomerization reactions is a hydride mechanism in which the catalytic conversion starts with a metal hydride species. The Shell Higher Olefin Process (“SHOP”) is efficient in a product range from C4 to C20.[13] If single olefins instead of product mixtures are the desired targets, other metal catalysts or systems have to be employed. Especially the selective di-, tri- and

tetramerization of ethylene selectively yield the preferred olefins (C4, C6 or C8); a small selection of processes will be mentioned in this chapter. During the "Alphabutol-Process" ethylene gets dimerized by a titanium catalyst with 1-butene as the dominating product. 23 plants worldwide work with this licensed process.[14] The selective trimerization was discovered as a side reaction during the polymerization of ethylene from Manyik at Union Carbide Corporation.[15] Some of the ethylene is trimerized to 1-hexene, which then co-polymerizes with ethylene forming a polymer containing butyl side chains. Noticeable differences in temperature and pressure dependence were observed. Based on many results and catalytic studies, the authors concluded that 1-hexene was produced via a mechanism other than linear chain growth and they proposed a metallocycle mechanism.[11] Over the years, many catalytic systems were found to be active for the selective trimerization of ethylene. Currently, the Phillips Petroleum catalyst system (discovered by Reagan) is the only example of a commercial scale ethylene trimerization plant.[16] Chevron Phillips recently successfully commercialized this technology in Quatar in 2003, which bases on a chromium – pyrrolyl - aluminum system.[16] Following up on his encouraging results for the co-polymerization of CO and ethylene, Wass (British Petroleum) discovered in 2002 that chromium complexes containing P-ortho-methoxyaryl PNP ligands can also be used for the selective trimerization of ethylene after activation with MAO.[17] Further investigations on these PNP catalysts by Bollmann (Sasol) revealed that selective tetramerization of ethylene yielding 1-octene was possible with various ligand systems that were structurally related to Wass´ trimerization system.[18] While a broad spectrum of chelating ligands from the type P-P-P, P-N-P, S-N-S or cyclopentadienyl can be employed, most of the systems focus on chromium as central metal.

Especially the dimerization of propylene or 1-butene plays a central role for the formation of gasoline with a high octane number. As a result, branched hexenes or octenes can be obtained and used for gasoline blending. The Dimersol process (*Institut Francais du Pétrole* IFP) is of great industrial and technical interest.[19] It makes use of a nickel-aluminum system in the absence of any phosphine ligand (non-regioselective propylene dimerization). The system is one of very few refinery technologies where an applied industrial process is based on a homogeneous organometallic catalyst.[20,21] Different variants of this process are developed for several olefinic feedstocks.

To avoid the problems of product separation under homogeneous conditions, Chauvin and co-workers reported the dimerization of propylene in chloroaluminate Ionic Liquids.[22] The IFP recently established this biphasic system named Difasol for the dimerization of propylene with high selectivities.[23] The Difasol technique can be retrofitted to existing Dimersol plants to enhance conversion and selectivity.

The desire for green solvents in industrial processes has certainly been the germ for the crystallization of attention around Ionic Liquids. Ionic Liquids turned to be new materials that not only play the role of solvents but also provide new properties and make new applications available.

While propylene and 1-butene dimerization processes are interesting as additives for gasoline, 1-pentene and 1-hexene dimerization products are attractive diesel fuel additives.[24] The Cetane Number (CN) gives a rate for the ability of ignition in diesel fuel engines.[25] Because of the self ignition of diesel fuel in the compressed air of an engine (700-900°C), higher CN means lower combustion temperatures and this results in cleaner combustions and lower emissions. While 1-hexene has a CN of 27, the dimerization product 1-undecene has 65 and the trimerization product 1-octadecene has 71.[26]

Finally, it is clear that catalysis as a science is as young, exciting and vibrant as it was at the beginning of last century, when the foundations for this important part of chemistry were laid. Mittasch recognized the enormous future significance after scanning 3000 different materials for the ammonia process:

“Chemistry without catalysis would be like a sword without a handle, like a lamp without light and like a bell without a ring.”[27]

In this thesis, highly efficient systems for the catalytic dimerization of α-olefins, especially propylene, were investigated. The aim of the work was to address problems of current research. One of the objectives of this work was the synthesis of new bis(imino)pyridine vanadium(III) complexes with different substitution patterns to understand and control the selectivity of the formed dimerization products. A second goal was to optimize the activity and the catalyst lifetime under homogeneous and heterogeneous conditions. Furthermore it was of interest to solve the problem of product separation under homogeneous conditions and to create a catalytic system which is able to run under homogeneous and heterogeneous settings.

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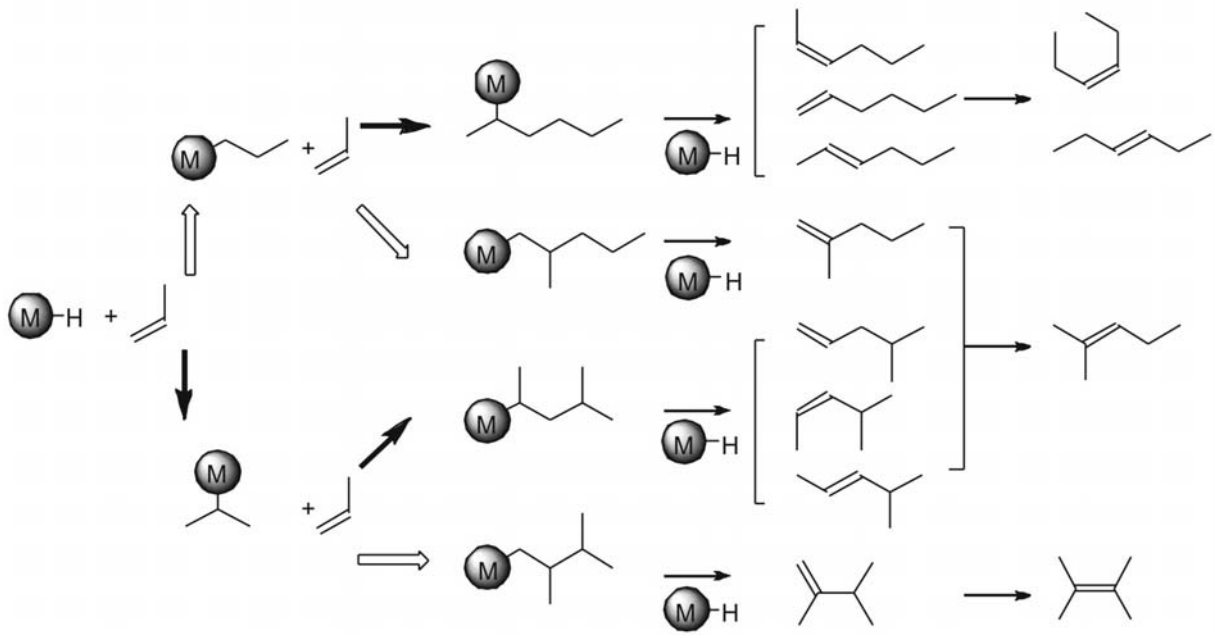
3. Overview of Thesis Results

This thesis comprises four publications, which are presented in chapters 4 to 7.

3.1. Homogeneous catalytic dimerization of propylene with bis(imino)-pyridine vanadium(III) complexes

The first chapter of this thesis is dedicated to the synthesis and characterization of a series of new bis(imino)pyridine vanadium(III) complexes, by changing the substitution pattern of the aniline moiety. They were tested for the homogeneous catalytic dimerization of propylene after activation with MAO. During this dimerization reaction 12 different hexene isomers can be formed. The aim of the work was to control the selectivity with substitution patterns at the ligand, or with the use of additives.



Scheme 1. Dimerization products of propylene and catalytic cycles.

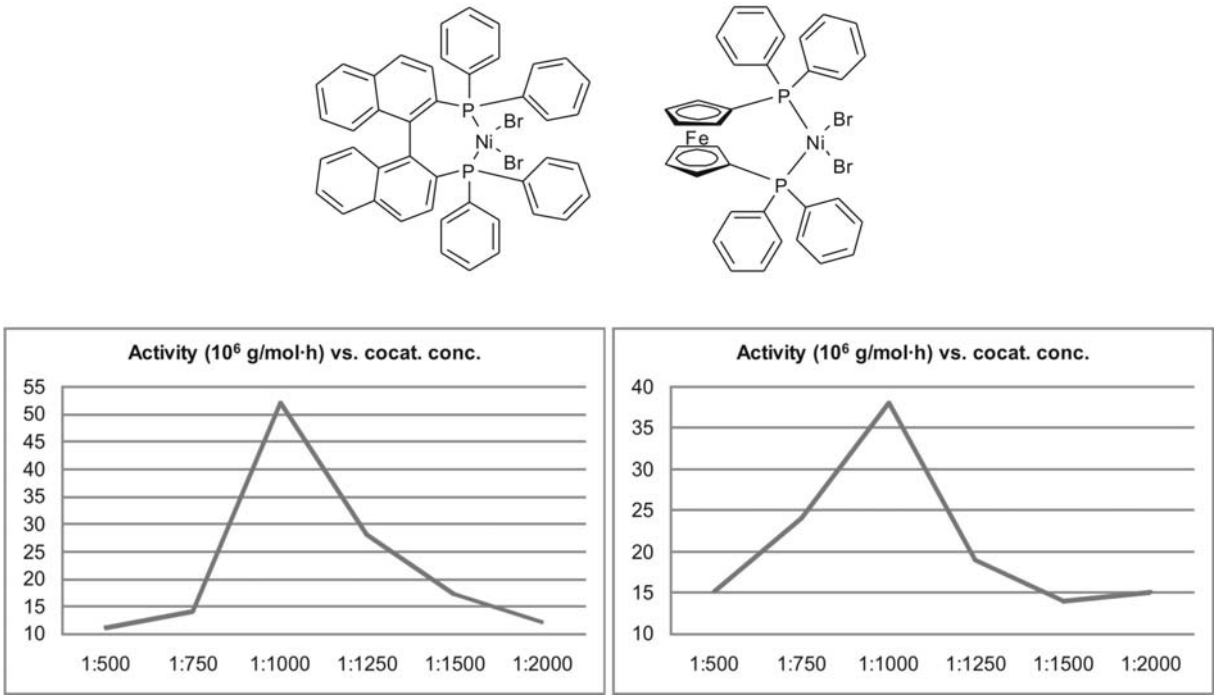
Bulky substituents on the ortho position had positive influence on the selectivity of the dimer products. The use of additives had an enormous influence on the product distribution. It changed from 90 % of 1,2-insertion up to 78 % for 2,1-insertion with the

use of 2.5 equiv. of PPh_3, for the first insertion step. The presence and the amount of additive played an important role in the formation of hexenes.

3.2. Highly active dimerization of olefins using nickel phosphine catalysts

The bis(imino)pyridine vanadium(III) system showed high selectivities but only medium activities. A nickel bromide system with bulky chelating phosphine ligands and $EtAlCl_2$ as cocatalyst showed a better performance.

The systematic variation of the catalyst to cocatalyst ratio under homogeneous conditions led to optimized catalytic reaction conditions. With this maximum of activity, catalyst life time experiments were performed. After seven repetitions of the dimerization experiments, the catalysts showed high activities of up to 87 % of the starting activity.



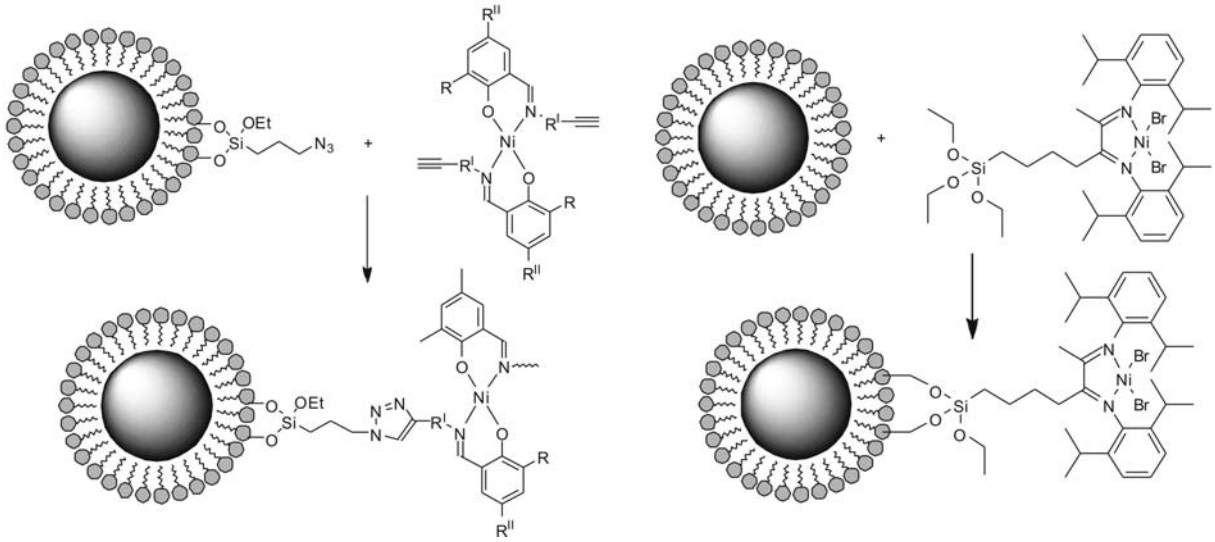
Scheme 2. Catalyst activities of the dimerization of propylene with the complexes above and various $EtAlCl_2$ ratios.

Herein we report the application of the two nickel phosphine complexes in a fixed bed reactor. In contrast to homogeneous reactions in a closed system, the heterogeneous open system is fitted with a continuous flow of the educts. This resulted in shorter

contact times between catalyst and olefin and had a tremendous effect on the product selectivity. In both experiments the amounts of dimer products were constantly 100%. These results underline the potential of the nickel phosphine system under homogeneous and heterogeneous conditions.

3.3. Practical heterogeneous complexes and their application as magnetically separable olefin dimerization catalysts

To avoid the problems of product separation under homogeneous conditions, a magnetically separable catalyst was introduced. The idea was to develop a simple synthetic protocol for a serious of ligand or complex structures. Highly active nickel catalysts known for the polymerization of ethylene or dimerization of propylene after activation with MAO were substituted with functional groups and combined with core shell particles. The magnetic core allowed to separate these particles by the means of a magnetic field. This permits to work under homogeneous conditions with the advantages of heterogeneous catalysis.

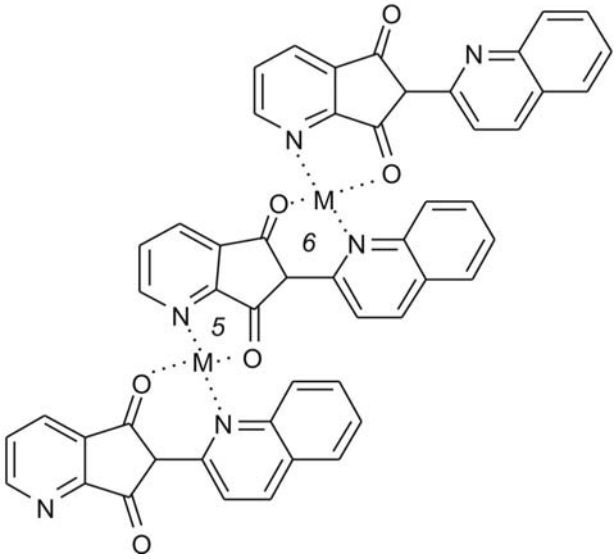


Scheme 3. Route of heterogenization of phenoxyimine (left side) and bisimine (right side) nickel complexes.

The synthesized particles were characterized by TEM, SEM and EDX spectroscopy. Interestingly, all dimerization reactions showed high selectivities towards dimer products. Furthermore, the reaction products of the homogeneous and heterogeneous catalysts were the same.

3.4. Highly efficient olefin dimerization catalysts

The next step was to create a variable and flexible system for the dimerization of the α-olefins C_3-C_6 and *cis*-butene. The special coordination sites of the ligand allows various binding modes to different central metals. The early and late transition metals titanium, cobalt and nickel were combined in different ratios with the potential ligand and tested in dimerization reactions after activation with MAO.



Scheme 4. Possible coordinating states; five and six membered rings and possible super lattices.

The variation of the central metal resulted in differences of the catalyst selectivity. While nickel complexes provided the highest activities for the short chain olefins propylene and 1-butene, titanium complexes were more active for the higher olefins 1-pentene and 1-hexene. Furthermore the activation ratio (M:Al) was of interest. Raising the activation ratio from 1:500 to 1:1000 (M:Al) increased the activities of the dimerization experiments. In all runs, no high molecular weight products were observed.

3.5. Individual Contribution to Joint Publications

The results presented in this thesis were obtained in collaboration with others and are published, accepted or to be submitted as indicated below. In the following, the

contributions of all the co-authors to the different publications are specified. The asterisk denotes the corresponding author.

Chapter 4

This work is published in *Journal of Molecular Catalysis A: Chemical* 322 (2010) 45–49 with the title

"Homogeneous catalytic dimerization of propylene with bis(imino) pyridine vanadium(III) complexes"

Julian R.V. Lang, Christine E. Denner, Helmut G. Alt*

I performed all catalytic studies, syntheses and characterizations presented in this work and wrote the publication. Christine Denner and Helmut Alt supervised this work and were involved in scientific discussions, comments and correction of the manuscript.

Chapter 5

This manuscript has been submitted for publication in *Journal of Molecular Catalysis A: Chemical* with the title

"Highly active dimerization of olefins using nickel phosphine catalysts"

Julian R.V. Lang, Helmut G. Alt*

I performed all catalytic studies, syntheses and characterizations presented in this work and wrote the publication. Helmut Alt supervised this work and was involved in scientific discussions, comments and correction of the manuscript.

Chapter 6

This manuscript is to be submitted with the title

"Practical Heterogeneous Complexes and their Application as Magnetically Separable Olefin Dimerization Catalysts"

Julian R.V. Lang, Thomas Ruhland, Helmut G. Alt*, Axel H. E. Müller

I synthesized all complexes and supported catalysts and performed all reactions. Also, the publication was written by me. The syntheses of the silica shell nano particles and the characterizations of all particles and heterogeneous complexes presented in this work were done by Thomas Ruhland. Helmut Alt and Axel Müller supervised this work and were involved in scientific discussions, comments and correction of the manuscript.

Chapter 7

This manuscript is to be submitted with the title
“Highly efficient olefin dimerization catalysts”
Julian R.V. Lang, Julia Ewert, Helmut G. Alt*

All catalytic studies in this work were performed by me and the publication was written by me. Julia Ewert helped with the development of the dimerization protocol during her lab course. Helmut Alt supervised this work and was involved in scientific discussions, comments and correction of the manuscript.

4. Homogeneous catalytic dimerization of propylene with bis(imino) pyridine vanadium(III) complexes

Julian R.V. Lang[a], Christine E. Denner[a], Helmut G. Alt[a]*

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Abstract: A series of new bis(imino)pyridine vanadium(III) complexes was synthesized. They were tested for the homogeneous catalytic dimerization of propylene after activation with MAO. The activity and selectivity depends on the ligand structure of the corresponding organic coordination compound. The influence of PPh_3 as an additive was investigated and high dependency could be observed.

Keywords: Homogeneous Catalyst, Vanadium, Bis(imino)pyridine, Propylene, Dimerization

Published in: *Journal of Molecular Catalysis A: Chemical* 322 (2010) 45–49.

4.1. Introduction

Unsatured short chained hydrocarbons are low priced educts for polymerization, oligomerization and metathesis application, produced by unselective thermal cracking processes.[1] Especially the dimerization of propylene play an important role for the formation of gasoline with a high octane number. As a result branched hexenes can be obtained and used as gasoline blending compounds. The Research Octane Number (RON) rises with the number of branching,[2-6] from RON = 96-99 for methylpentenes to 101 for dimethylbutene.[2, 7-8] Linear hexenes are in the range from 73-94 and play no role as additives for gasoline improvement. With the ban of lead-alkyl compounds and methyl-*tert*-butyl as anti knocking agent ether from gasoline, branched hydrocarbons represent a very important class of compounds for gasoline reformulation.[9]

The invention of highly active iron- and cobalt based olefin polymerization catalysts in the late 1990s has led to much interest in the chemistry of transition metal complexes bearing tridentate bis(imino)pyridine ligands.[10-21] These types of complexes were applied by Gibson and Brookhart in 1998 and great progress has been achieved since then. It is well established that bis(imino)pyridine iron(III) complexes show high activities and selectivites for the oligo- and polymerization of ethylene after activation with methyl aluminoxane (MAO). Several complexes with various metal centers and different ligand structures were published and many studies have reported the effects of ligand substitution patterns on activity and selectivity.[19-23] Bis(imino)pyridine vanadium(III) complexes were found to be selective for the oligomerization of ethylene to give linear olefins.[13, 24-26] These facts underline the importance of such catalysts.

Here we report the application of bis(imino)pyridine vanadium(III) complexes combined with MAO as cocatalyst in the selective dimerization of propylene. The influence of phosphorous containing additives is another aspect in this work.

4.2. Results and Discussion

*4.2.1. Synthesis of the bis(imino)pyridine compounds **1a-d***

The bis(imino)pyridine ligand precursors were synthesized via a condensation reaction (Scheme 1) of 2,6 diacetylpyridine with the respective aniline according to the literatures.[27]

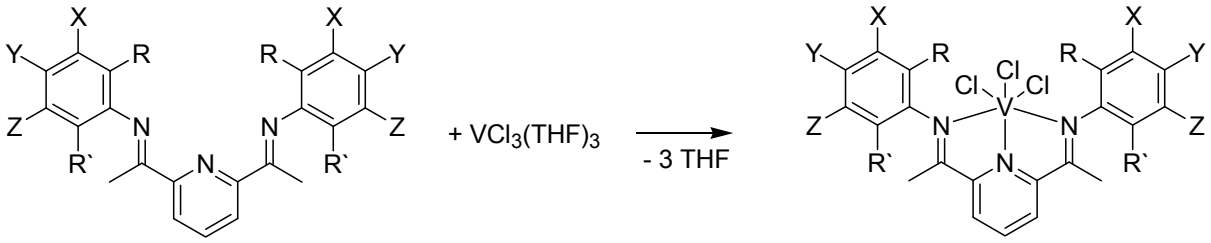
1a R = R`= Z = H, X = F, Y = Me
1b R = R`= Z = H, X = Cl, Y = Me
1c R = R`= Z = H, X = Br, Y = Me
1d R = R`= H, X = Z = Br, Y = Me

Scheme 1. Synthesis of the bis(imino)pyridine compounds **1a-d**.

The yields of the compounds **1a-d** are generally high (up to 94%).

*4.2.2. Synthesis of the complexes **2-5***

The complexes were synthesized via an addition reaction (Scheme 2) of the vanadium(III)trichloride THF adduct and the respective bis(imino)pyridine compound in diethyl ether. The resulting complexes were obtained in good yields (65-87%).



2 R = R`= Z = H, X = F, Y = Me
3 R = R`= Z = H, X = Cl, Y = Me
4 R = R`= Z = H, X = Br, Y = Me
5 R = R`= H, X = Z = Br, Y = Me

Scheme 2. Synthesis of the bis(imino)pyridine vanadium(III) complexes **2-5**.

The listed complexes **2-28** were all tested for their catalytic activities in dimerization reactions (Table 1).

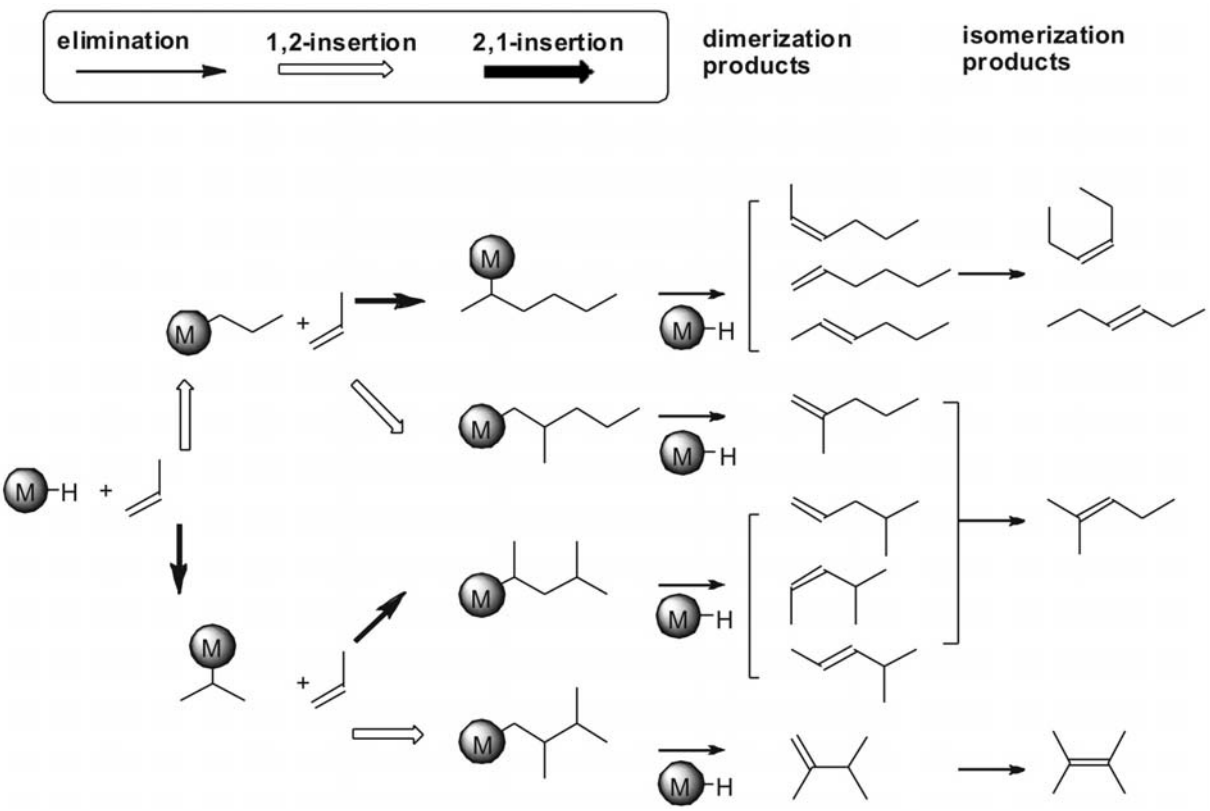
Table 1. Synthesized complexes **2-28**. Complexes **6-28** were already reported in the literature.[25] Compounds **2-5** are new.

V(III) complex no.	R	X	Y	Z	R`
2	H	F	methyl	H	H
3	H	Cl	methyl	H	H
4	H	Br	methyl	H	H
5	H	Br	methyl	Br	H
6	H	H	Cl	H	H
7	H	H	I	H	H
8	H	H	NO_2	H	H
9	methyl	H	I	H	H
10	methyl	H	methyl	H	methyl
11	methyl	H	H	H	H
12	ethyl	H	H	H	H
13	*iso*-propyl	H	H	H	H

14	*tert*-butyl	H	H	H	H
15	propyl	H	H	H	H
16	benzyl	H	H	H	H
17	*iso*-propyl	H	H	H	methyl
18	*iso*-propyl	H	H	H	*iso*-propyl
19	methyl	H	methyl	H	H
20	H	H	butyl	H	H
21	methyl	methyl	H	H	H
22	methyl	H	H	H	Cl
23	methyl	H	H	methyl	H
24	H	H	Br	H	H
25	methyl	H	Cl	H	H
26	methyl	H	H	H	methyl
27	H	H	F	H	H
28	methyl	Cl	H	H	H

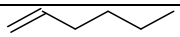
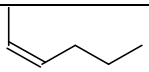
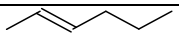
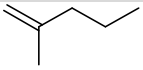
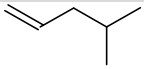
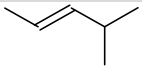
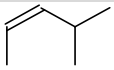
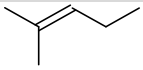
4.2.3. Catalytic dimerization reactions of propylene

Various bis(imino)pyridine vanadium(III) compounds were tested for the dimerization of propylene after activation with MAO (V:Al = 1:500) to give hexene isomers. The catalytic activities and selectivities of the corresponding catalysts are important aspects. The activity was determined by the weight increase of the reaction vessel after removing the propylene. While high activities for the oligo- and polymerization of ethylene were achieved with this type of catalyst,[25, 28] the results with propylene varied in the range of 95–215 kg/mol h (TOF = 1130-2560 h^{-1}). For our application, it is more important to have a look at the selectivities and product distributions.



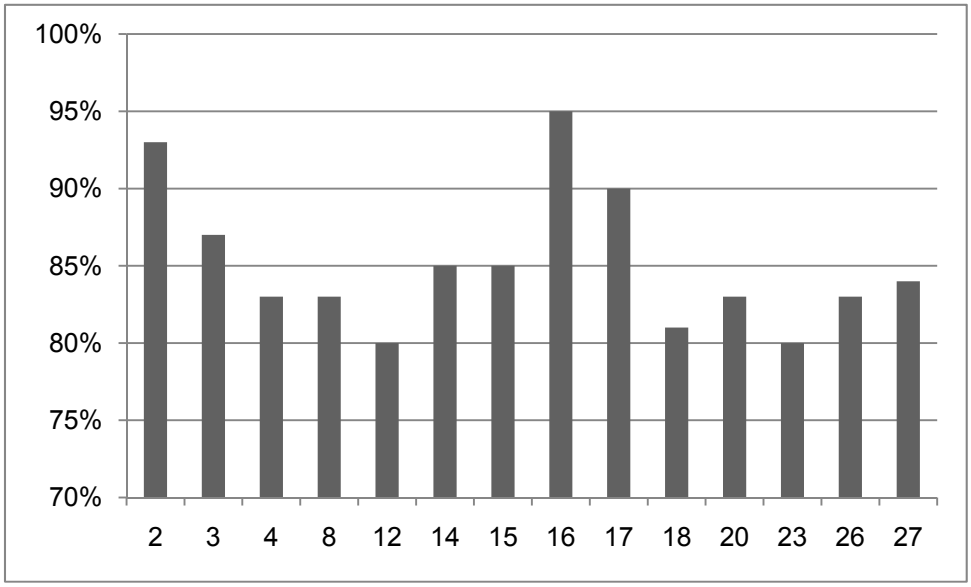
Scheme 3. Dimerization products of propylene and catalytic cycles.

Table 2. All hexene isomers with full names and abbreviations.

Isomer				
Name/ Abbreviation	1-hexene 1-hex	cis-2-hexene c-2-hex	trans-2-hexene t-2-hex	cis-3-hexene c-3-hex
Isomer				
Name/ Abbreviation	trans-3-hexene t-3-hex	2-methyl-1-pentene 2-MP-2	4-methyl-1-pentene 4-MP-1	trans-4-methyl-2-pentene t-4-MP-2
Isomer				
Name/ Abbreviation	cis-4-methyl-pentene c-4-MP-2	2-methyl-2-pentene 2-MP-2	2,3-dimethyl-1-butene DMB-1	2,3-dimethyl-2-butene DMB-2

The dimerization of propylene can lead to 12 hexene isomers via coordination, double insertion and elimination reactions (Scheme 3). The names and abbreviations of all isomers are listed in Table 2.

It is obvious that complexes **14-17** with bulky ligands like alkyl/aryl substituents on positions 2 or 6 (ortho position) of the imine fragment (scheme 4), achieve high selectivities up to 95 % (**16**). Bulky substituents on both sides have a negative effect. The selectivity falls from 90 to 81 % with the replacement of methyl (**17**) to *iso*-propyl (**18**). Moreover, steric hindrance in ortho position has an influence on the product distribution. While complexes **11-13** produce 4-methyl-1-pentene as main product, bulky substituents shift it to 2-methyl-1-pentene. These bulky groups favor 1,2-insertion as an initial step.



Scheme 4. Catalysts **2-4, 8, 12, 14-18, 20, 23, 26** and **27** with the highest selectivity towards dimerization products of propylene.

A substitution with halides on the para position has a great influence on the formation of hexenes. Compared to complex **11** (main product 4-methyl-1-pentene with a selectivity of 62 %), a halide substitution gives 4-methyl-1-pentene with selectivities between 74 % (**25**) and 82 % (**9**).

The selectivity of the formation of hexene isomers decreases in the following manner F (93%) (**2**) > Cl (87%) (**3**) > Br (83%) (**4**) on the meta position (scheme 4). The *β*-hydrogen elimination is favored by electron withdrawing groups compared to the heavier homologue halides. The distribution of the dimeric products is nearly the same for all three halide substituted complexes with 4-methyl-1-pentene as main

product and selectivities up to 90% are observed (Table 3). With the high dimer and product selectivity of **2**, 4-methyl-1-pentene is produced with a total amount of 83 %. Electron withdrawing or pushing groups on position 4 of the imine fragment have no influence on the dimer selectivity (**6-8**, **20**, **24** and **27**). The difference is obvious in product distribution. Complex **20** with a withdrawing group produces 2-methyl-1-pentene with 47 %. On the other side, electron pushing groups generate 4-methyl-1-pentene with an amount of up to 75 %.

The kind of substitution at the meta position of the bis(imino)pyridine complex has no influence on the selectivity of the dimers, but it effects the distribution of the dimers immensely. Complexes **6-9, 24, 25** and **27** with a –J-effect at the meta position of the phenyl group give a maximum selectivity of 2-methyl-1-pentene of 13 %. A ligand with a +J-effect at the same position give complex **20** which shows a selectivity for 2-methyl-1-pentene of 47 %. The formation of 4-methyl-1-pentene shows its highest selectivity (90%) (**2**) in contrast to the formation of 2-methyl-1-pentene by the reaction of complexes with a –J-effect at the ligand precursor like Cl, Br or I.

These two products are generated by different first insertion steps (scheme 3), and are caused by the electronic influence of both substituents. Complex **5** is the only complex that produces 2,3-dimethylbutene in satisfying yields (25 %) with medium selectivity towards dimerization products (Table 3).

Table 3. Selectivity of dimerization products and product distribution within hexene isomers for the vanadium(III) complexes **2-28**.

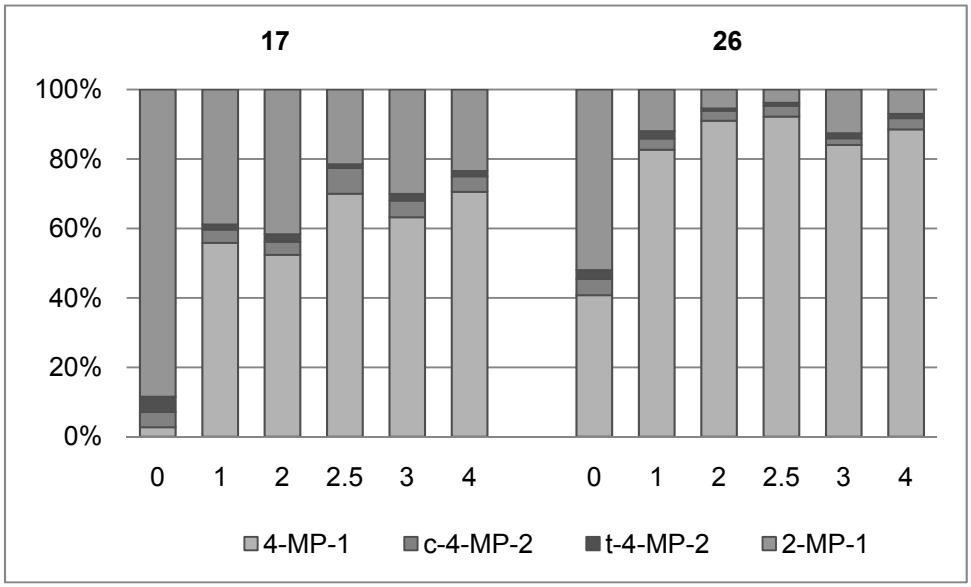
V(III) complex no.	**Selectivity to dimers (%)**	**Products within the dimers (%)**							
		4-MP-1	2,3-DMB-1	c-4-MP-2	t-4-MP-2	2-MP-1	t-2-hex	2-MP-2	c-2-hex
2	93	90	1	4	-	5	-	-	-
3	87	85	2	6	3	4	-	-	-
4	83	89	1	7	1	2	-	-	-
5	60	24	25	45	0	6	-	-	-
6	70	68	5	14	3	9	-	1	-
7	72	71	2	13	2	8	-	4	-
8	83	73	5	3	3	13	-	3	-
9	75	82	-	9	3	6	-	-	-
10	55	73	-	7	-	20	-	-	-
11	55	62	2	18	4	14	-	-	-
12	80	68	2	14	5	10	1	-	-

13	60	55	-	13	3	26	3	-	1
14	85	5	-	8	11	75	1	-	-
15	85	36	-	10	6	46	1	1	-
16	95	7	-	7	6	80	-	-	-
17	90	3	-	4	5	88	-	-	-
18	81	11	-	5	7	77	-	-	-
19	75	8	-	7	9	76	-	-	-
20	83	19	5	15	7	47	1	6	1
21	76	34	1	10	8	45	1	1	1
22	70	32	2	10	4	52	-	-	-
23	80	25	-	7	5	63	-	-	-
24	77	70	-	17	2	6	-	5	-
25	40	74	1	13	4	8	-	-	-
26	83	41	-	5	3	51	-	-	-
27	84	75	3	9	3	6	-	4	-
28	77	72	2	14	6	6	-	-	-

4.2.4. Influence of PPh_3 as an additive

In the late 60s Wilke recognized the influence of additives in catalytic reactions.[29] Phosphanes are widely used additives and a positive influence on selectivity and activity was observed during dimerization of propylene.[30]

The relevant complexes were dissolved in toluene, PPh_3 was added in a ratio of metal:additive = 1:1, (2, 2.5, 3 and 4). The solutions were stirred for 30 min and activated with MAO.



Scheme 5. Product distribution of the reaction of the complexes **17** and **26** and propylene with a various ratio of the additive PPh_3.

The addition of the additive had a positive influence on the dimer selectivity (90 %) with the use of 2 eq. PPh_3 for **17** The selectivity could be improved up to 95%. For all other amounts no improvement could be observed. In contrast, the use of additive had a great influence on the product distribution (Scheme 5). With the addition of 2.5 equiv. a maximum of 70 % for the formation of 4-methyl-1-pentene (**17**) could be achieved. The absence of PPh_3 effects the formation of 2-methyl-1-pentene with a selectivity of 88%. Insertion mechanisms are influenced by the use of phosphine containing additives, which results in an 1,2-insertion instead of 2,1-insertion. The results of the corresponding reactions of complex **26** (Scheme 5) confirm the additive dependency as discussed before. A selectivity of 90 % was detected for 4-methyl-1-pentene by the addition of 2-2.5 mole PPh_3 in contrast to 51 % without an additive.

4.3. Summary and Conclusion

Novel complexes of the type bis(imino)pyridine vanadium(III) (**2-5**) were synthesized. Because of the simple synthetic route, numerous substitution patterns can be performed. Bulky substituents on the ortho position have positive influence on the selectivity of the dimer products. Complex **16** with a benzyl substituent at the ortho position gave a selectivity of 95 % for dimers. Substituents at the 2 and 6 positions of

the phenyl group accrue the 1,2-propylene insertion. Different halide groups as substituents on the para position have no influence on the product distribution and selectivity. Effects can be obtained when electron withdrawing and donating groups are introduced. The first ones generate 4-methyl-1-pentene as main product. Electron pushing substituents give 2-methyl-1-pentene. The octane numbers of the main products are between 94 and 99. It is obvious, that the structure of the precatalyst, in particular the substitution pattern of the organic compound has a great influence on the product distribution, but not on the selectivity. No dependence for dimer selectivity is obvious from the insertion pathway. In less cases the expected multiple branched hexenes could be obtained. Complex **5** produced 2,3-dimethylbutene in yields of 25% within the dimerization products. The use of additives had a positive influence on the product distribution and was very selective for complex **26**. Complex **26** and 2 equiv. of the additive PPh_3 produced 90% of 4-methyl-1-pentene within the dimers. In the case of complex **17** the use of an additive had an enormous effect on the initial insertion step. It changed from 90 % of 1,2-insertion up to 78 % for 2,1-insertion with the use of 2.5 equiv. of PPh_3.

4.4. Experimental Section

4.4.1. General considerations

Air- and moisture sensitive reactions were carried out under an atmosphere of purified argon using conventional Schlenk or glove box techniques. The dimerization reactions were performed with pressure Schlenk tubes.

The products of the dimerization experiments were characterized by a gas chromatograph (Agilent 6890) and GC/MS (FOCUS DSQ^{TM} Thermo Scientific). Mass spectra were recorded on a Varian MAT CH7 instrument (direct inlet system, electron impact ionization 70eV). Elemental analyses were performed with a VarioEl III CHN instrument. Acetanilide was used as standard. NMR spectra were taken on a Varian Inova 400 instrument. The samples were prepared under argon atmosphere and measured at room temperature. Chemical shifts (δ, ppm) were recorded relative to the residual solvent peak at δ = 7.24 ppm for chloroform-*d*. The multiplicities were assigned as follows: s, singlet; m, multiplet; t, triplet. ^{13}C {^{1}H} NMR spectra were fully

proton decoupled and the chemical shifts (δ, ppm) are relative to the solvent peak (77.0 ppm).

4.4.2. Materials

All solvents were purchased as technical grade and purified by distillation over Na/K alloy under an argon atmosphere. All other chemicals were purchased commercially from Aldrich or Acros or were synthesized according to literature procedures. The methyl aluminoxan solution (MAO, 30wt.% in toluene) was obtained from Albemarle, USA.

4.4.3. General procedure for the synthesis of the preligands

10 g mole sieves (4Å) and 0.5 g of catalytically active SiO_2/Al_2O_3 pellets were added to a solution of 0.49 g (3.0 mmol) diacetylpyridine in toluene. After addition of 7.0 mmol of the respective aniline, the solution was heated at 45°C for 24 hours. After filtration over Na_2SO_4 and evaporation to dryness, the products were precipitated as yellow solids from methanol over night at -20°C (73-94%).
Spectroscopic data:
1a: ^{1}H NMR (400 MHz, $CDCl_3$): 8.30 (d, 2H, Py-H_m), 7.85 (t, 1H, Py-H_p), 7.15 (t, 2H, Ph-H), 6.53 (m, 4H, Ph-H), 2.39 (s, 6H, N=C_{Me}), 2.26 (s, 6H, Ph-CH_3). 13C {1H} (100.5 MHz, $CDCl_3$): 167.9 (Cq), 163.1 (Cq), 159.9 (Cq), 155.3 (Cq), 150.4 (Cq), 136.9 (CH), 131.6 (CH), 122.4 (CH), 114.8 (CH), 106.6 (CH), 16.2 (CH_3), 14.1 (CH_3). MS data: 377 ($M^{\bullet+}$) (88), 362 (12), 150 (100).
1b: ^{1}H NMR (400 MHz, $CDCl_3$): 8.30 (d, 2H, Py-H_m), 7.8t (t, 1H, Py-H_p), 7.21 (d, 2H, Ph-H), 6.87 (s, 2H, Ph-H), 6.64 (d, 2H, Ph-H), 2.40 (s, 6H, N=C_{Me}), 2.36 (s, 6H, Ph-CH_3). 13C {1H} (100.5 MHz, $CDCl_3$): 168.0 (Cq), 155.3 (Cq), 150.1 (Cq), 134.5 (Cq), 130.9 (Cq), 136.8 (CH), 131.2 (CH), 122.4 (CH), 119.8 (CH), 117.8 (CH), 19.4 (CH_3); 16.3 (CH_3). MS data: 409 ($M^{\bullet+}$) (52), 166 (100).
1c: ^{1}H NMR (400 MHz, $CDCl_3$): 8.30 (d, 2H, Py-H_m), 7.85 (t, 1H, Py-H_p), 7.21 (d, 2H, Ph-H), 7.06 (s, 2H, Ph-H), 6.70 (d, 2H, Ph-H), 2.40 (s, 6H, N=C_{Me}), 2.39 (s, 6H, Ph-CH_3). 13C {1H} (100.5 MHz, $CDCl_3$): 168.1 (Cq), 155.2 (Cq), 150.1 (Cq), 132.7 (Cq), 124.9 (Cq), 136.8 (CH), 131.0 (CH), 123.0 (CH), 122.4 (CH), 118.4 (CH), 22.2 (CH_3), 16.3 (CH_3). MS data: 499 ($M^{\bullet+}$) (52), 484 M–Me (8), 210 CH_3C=NAr (100).

1d: ^{1}H NMR (400 MHz, $CDCl_3$): 8.48 (d, 2H, Py-H_m), 8.07 (t, 1H, Py-H_p), 7.24-7.44 (m, 4H, Ph-H), 2.76 (s, 6H, Ph-CH_3), 2.62 (s, 6H, N=C_{Me}). 13C {1H} (100.5 MHz, $CDCl_3$): 169 (Cq), 155 (Cq), 151 (Cq), 132.0 (Cq), 125.2 (Cq), 137.0 (CH), 129 (CH), 122.7 (CH), 23.0 (CH_3), 16.5 (CH_3). MS data: 657 ($M^{\bullet+}$) (52), 577 M–Br (17), 290 M–$CH_3C{=}N_{Ar}$ (100).

4.4.4. Synthesis of the bis(imino)pyridine vanadium(III) complexes

An amount of 0.22 mmol of the respective bis(imino)pyridine compound was dissolved in 20 ml diethylether and stirred. A stoichiometric amount of vanadium trichloride-tetrahydrofuran adduct was added at room temperature. Stirring was continued overnight. Pentane was added to precipitate the product, which was subsequently collected by filtration, washed with pentane and dried in vacuo. The resulting solids were obtained with an overall yield of 65-87%.
Spectroscopic data:
2: MS data: 533 ($M^{\bullet+}$) (8), 497 M-Cl (100), 377 (30), 150 (62), 36 (100). $C_{23}H_{21}Cl_3F_2N_3V$ (533.02): calcd. C 51.66, H 3.96, N 7.86. Found C 49.87, H 4.34, N 7.02%.
3: MS data: 565 ($M^{\bullet+}$) (13), 531 M-Cl (100), 406 (18), 396 (10). $C_{23}H_{21}Cl_5N_3V$ (564.96): calcd. C 48.67, H 3.73, N 7.40. Found C 48.97, H 3.55, N 7.13%.
4: MS data: 653 ($M^{\bullet+}$) (7), 619 (37), 541 (10), 187 (63), 36 (100). $C_{23}H_{21}Cl_3Br_2N_3V$ (652.86): calcd. C 42.08, H 3.22, N 6.40. Found C 42.61, H 3.33, N 6.42%.
5: MS data: 808 ($M^{\bullet+}$) (4), 772 (100). $C_{23}H_{19}Cl_3Br_4N_3V$ (808.68): calcd. C 33.92, H 2.35, N 5.16. Found C 33.45, H 2.30, N 4.89%.

4.4.5. Homogeneous dimerization of propylene

The respective complex was dissolved in toluene and activated with MAO solution (V:Al = 1:500) and transferred into a 400 ml pressure Schlenk tube. The pressure Schlenk tube was filled with 50 ml liquid propylene and closed, warmed to room temperature with an external water bath and stirred. After the reaction time of 1 hour, the Schlenk tube was opened and the solution was analyzed by GC.

4.5. Acknowledgement

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5. Highly active dimerization of olefins using nickel phosphine catalysts

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Abstract: The catalytic dimerization of propylene and 1-butene with nickel phosphine complexes, after activation with $EtAlCl_2$, has been performed. The influence of the amount of the cocatalyst as well as the lifetime of the active catalyst were investigated. The selectivities of up to 94% (propylene) under homogeneous reaction conditions were improved to 100% dimer products when the reactions were performed heterogeneously in a fixed bed reactor. The catalysts showed very high activities for the dimerization of propylene ($52 \cdot 10^6$ g(dimer)/mol·h) and less activities for the dimerization of 1-butene ($7.3 \cdot 10^6$ g (dimer)/mol·h). The major products for the dimerization of 1-butene were linear octene isomers, with very high selectivities of 82%.

Keywords: Dimerization, Homogeneous catalyst, Heterogeneous catalyst, Propylene, 1- Butene

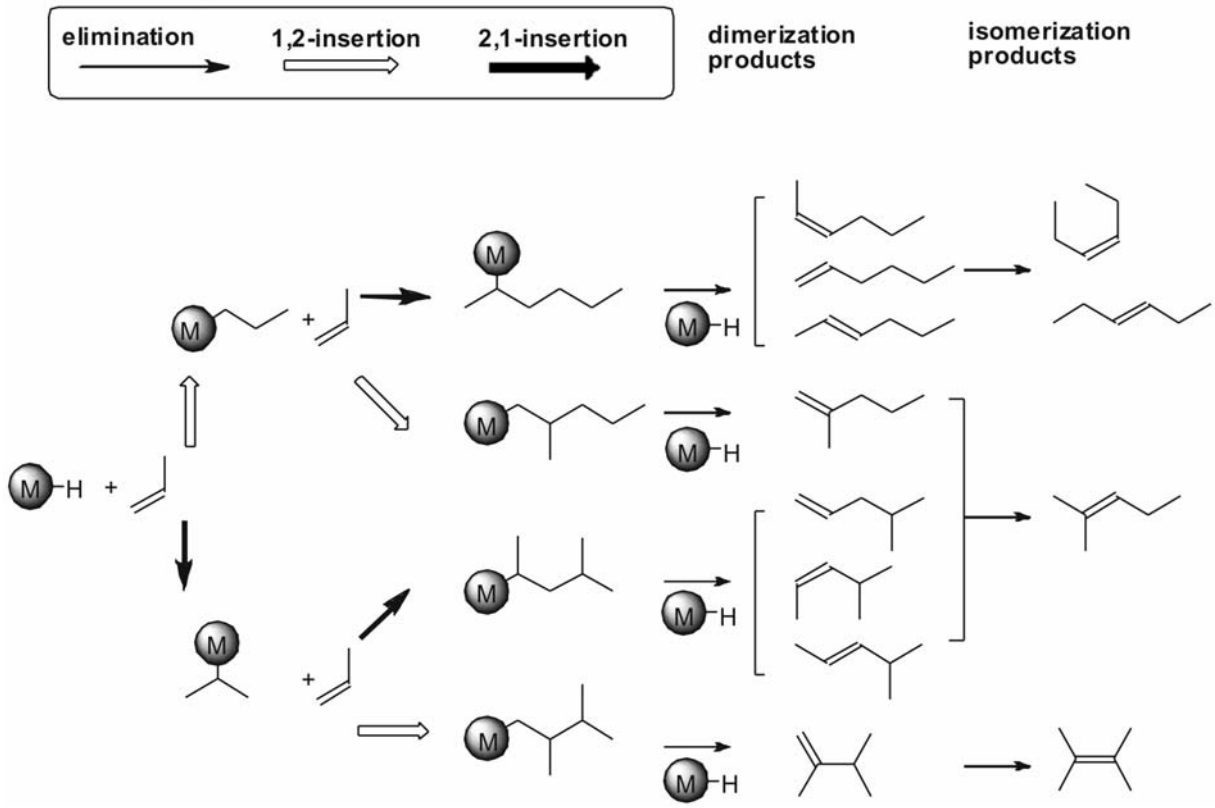
5.1. Introduction

α-Olefins can be produced by four main processes that operate either by elimination such as (i) cracking of paraffins, (ii) the dehydrogenation of paraffins, (iii) the dehydration of alcohols or by chain-growth reactions like (iv) oligomerization of olefins.[1] While polyolefin research initially focused on early transition metals, such as zirconium and titanium, there has been a change over the last decades to an increased highlighting on the late transition metals such as iron, nickel and palladium.[2-5] Reduced oxophilicity ease the handling and preparation of these complexes. The reactivity, selectivity and the ability to dimerize or oligomerize olefins is defined by the electronic, steric and chelating pattern of the ligand. Steric and

electronic properties of the surrounding ligand can be easily modified by ligand tailoring. The oligomerization of olefin is a major industrial process, and nickel complexes are the most frequently employed catalysts.[6] With ethylene as an easily available feedstock, many processes for the catalytic conversion to higher olefins were explored.[7] The Shell High Olefin Process (SHOP) is the most well known for the production of linear α-olefins and consists of a nickel(II)-based catalyst bearing a monoanionic P,O chelate.[1,8] Producing mostly C_4-C_{32} α-olefins, emphasis has been given mostly to the C_4-C_{20} range. These olefins are used for the production of detergents, plasticizers and co-monomers for linear low-density polyethylene (LLDPE).[2,9] Besides all the applications of ethylene oligomerization, propylene and 1-butene[10] are important educts for high octane gasoline components.

Especially the dimerization of propylene plays a central role for the formation of gasoline with a high octane number. As a result branched hexenes (Scheme1) can be obtained and used for gasoline blending. The Research Octane Number (RON) rises with the number of branching,[11] from RON= 96–99 for methylpentenes to 101 for dimethylbutenes.[12] Linear hexenes are in the range from 73 to 94 and play no role as additives for gasoline improvement. With the ban of lead-alkyl compounds and methyl-tert-butyl as anti-knocking agent ether from gasoline, branched hydrocarbons represent a very important class of compounds for gasoline reformulation.[13] In the late 60s, Wilke described a catalyst system containing a π-allylnickel complex in combination with a tertiary phosphine and a Lewis acid like aluminum trichloride producing mainly propylene dimers (80-85%).[14] The reduction of nickel acetylacetonate with alkylaluminum chlorides resulted in higher activities compared to the Wilke system.[15] The Dimersol process (*Institut Francais du Pétrole* IFP) is of great industrial and technical interest.[16] It makes use of a nickel-aluminum system in the absence of any phosphine ligand (non-regioselective propylene dimerization). The system is one of very few refinery technologies where a applied industrial process bases on a homogeneous organometallic catalyst.[17,18] Different variants of this process are developed for several olefinic feedstocks. For propylene, the system affords dimers with a selectivity of 80%, with 18% trimers and 2% tetramers as side products. The so called non regioselective dimerization gives 22% *n*-hexenes, 72% 2-methylpentenes and 6% 2,3-dimethylbutenes. In contrast, regioselective dimerization of propylene gives up to 85% of the desired highly branched hexene isomers. For this Sumitomo process, a nickel salt is combined with

tricyclohexylphosphine.[16,19] On the other hand the selectivity towards dimeric products shrinks to 59%.



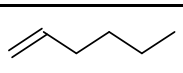
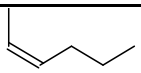
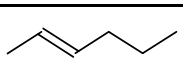
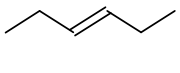
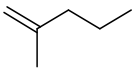
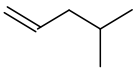
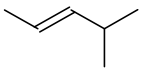
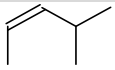
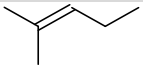
Scheme 6. Dimerization products of propylene and catalytic cycles.

The dimerization reactions can be controlled by the nature of the phosphines having different electronic and steric properties, so that different bite angles and intermediates can be formed.[16,20] All these nickel complexes show excellent activities. With π-allylnickel halides in combination with $EtAlCl_2$ in chlorobenzene, activities of up to 150 t(dimer)/g(Ni)h can be reached (extrapolated from -75 until -55°C to 25°C). These results are in the range of highly active enzymes.[20]

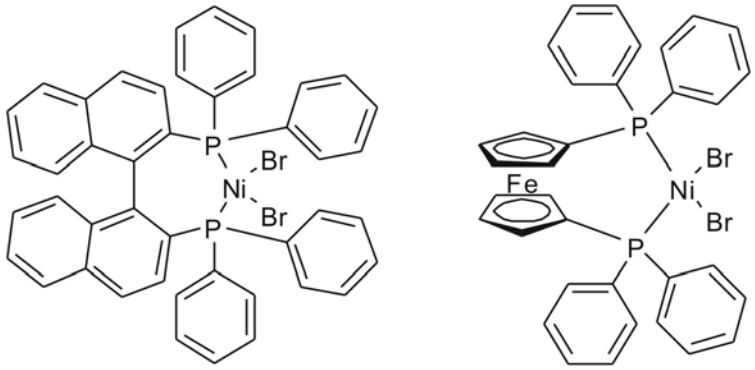
To avoid the problems of product separation under homogeneous conditions, Chauvin and co-workers reported the dimerization of propylene in chloroaluminate ionic liquids.[21,22] The IFP recently established this biphasic system named Difasol for the dimerization of propylene with high selectivities.[23] The Difasol technique can be retrofitted to existing Dimersol plants to enhance conversion and selectivity.

Most studies on homogeneous or biphasic systems having focused on monophosphine ligands for propylene dimerization, chelating diphosphines have been rarely employed.[16,24]

Table 1. All hexene isomers with full names and abbreviations.

Isomer				
Name/abbreviation	1-hexene 1-hex	cis-2-hexene c-2-hex	trans-2-hexene t-2-hex	cis-3-hexene c-3-hex
Isomer				
Name/abbreviation	trans-3-hexene t-3-hex	2-methyl-1-pentene 2-MP-1	4-methyl-1-pentene 4-MP-1	trans-4-methyl-2-pentene t-4-MP-2
Isomer				
Name/abbreviation	cis-4-methyl-pentene c-4-MP-2	2-methyl-2-pentene 2-MP-2	2,3-dimethyl-1-butene DMB-1	2,3-dimethyl-2-butene DMB-2

5.2. Results and Discussion



1 **2**

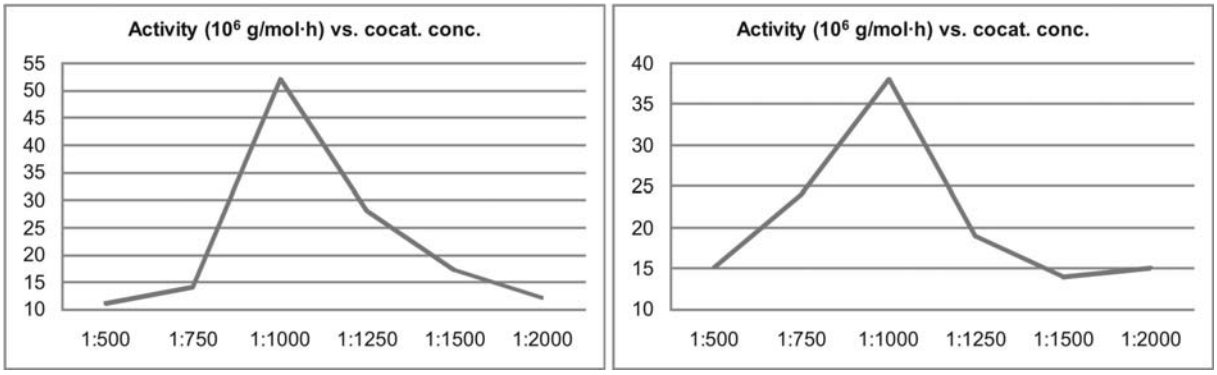
Scheme 7. Complexes 1 and 2 used for the dimerization reactions.

The performances in the catalytic propylene and 1-butene dimerization have been checked by varying the activation ratio, catalyst lifetime, nature of the α-olefin and the catalytic conditions (homogeneous or heterogeneous catalysis). Two complexes [(*S*)-BINAP]$NiBr_2$ (**1**) was prepared according to literature[25] and [1,1´-Bis(diphenylphosphin)ferrocene]nickel(II)bromide (**2**) was prepared by adaptions of published procedures[26] (both Scheme 2).

5.2.1. Homogeneous dimerization reactions with propylene

In the following section, we describe the catalytic dimerization of propylene under homogeneous conditions with a reaction time of one hour. The nickel phosphine complexes **1** and **2** were activated with an $EtAlCl_2$ solution to give hexene isomers. It is possible to obtain 12 hexene isomers during this coordination, double insertion and elimination step (Scheme 1, Table 1).

Investigations of the life time and the concentration dependency of the catalyst precursors **1** and **2** were the focus of this work. Complexes **1** and **2** were activated with $EtAlCl_2$ solution in different ratios. The activity towards dimerization of propylene is extremely influenced by the activation ratio. A ratio of 1:500 (Ni:Al) gave activities of $12 \cdot 10^6$ and $15 \cdot 10^6$ g(dimer)/mol(cat.)·h (**1** and **2**). A doubling to 1:1000 increased strongly the activity ($52 \cdot 10^6$ (TOF = 640,000 h^{-1}) and $38 \cdot 10^6$ g(dimer)/mol·h (TOF = 468,000 h^{-1})). It is obvious that the optimum performance of the activation ratio is 1:1000 (Ni:Al) (Scheme 3). These ultra high activities of complex **1** and **2** decrease with increasing amounts of cocatalyst. Depending on these results, the concentration ratio of 1:1000 (Ni: Al) was used as a standard condition for later lifetime experiments of the catalyst precursors **1** and **2** (Scheme 5).



Scheme 8. Activities of the dimerization of propylene with complex 1 (left) and 2 (right) and various $EtAlCl_2$ ratios.

Under homogeneous conditions the selectivity depends on the activity. An activation ratio of 1:500, effects high selectivities of 89 respectively 85 % (Table 2) towards dimeric products. The side products are trimeric or tetrameric products, but are not investigated closer. An increase of the amount of the cocatalyst reduces the relative yield of hexene isomers leading to 85 and 80 for the activation ratio of 1:1000. A

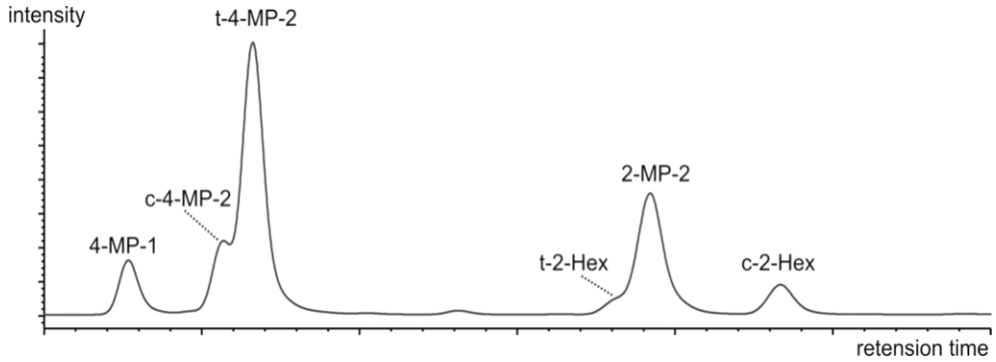
maximum of activity causes a minimum of the selectivity. The activation ratio of 1:2000 reflects the highest amount of dimers within the product phase. Very high results of 94 and 92 % were achieved with this relation. The selectivity and the activity can be controlled by the ratio of complex and cocatalyst. These variations can be caused by the conversion rate and the corresponding non coordinating counter ion of the cocatalyst. A constant amount of propylene was used for every experiment (50 ml). With higher conversion rates more dimers are produced and these act as educts for further coordination and dimerization reactions. At the end of the dimerization experiments after 1h (ratio 1:1000), no propylene was left in the pressure Schlenk tubes. This observation explains the relative low selectivity. An excess of the formed dimers leads to a coordination and insertion of dimers instead of propylene. Lower activities means lower conversion rates, followed by less time for side reactions. According to statistics, the catalyst prefers to coordinate and connect two propylene molecules instead of propylene and a hexene dimer. A further aspect is that the bulky hexenes block the insertion of further propylene.

Table 2. Dimerization of propylene with complexes 1 and 2. The amount of cocatalyst effects on the formation of the products.

complex	activation ratio Ni:$EtAlCl_2$	selectivity towards dimers [%]
1	1:500	89
1	1:750	88
1	1:1000	85
1	1:1250	87
1	1:1500	91
1	1:2000	94
2	1:500	85
2	1:750	83
2	1:1000	80
2	1:1250	89
2	1:1500	90
2	1:2000	92

The gas chromatograms of the dimerization experiments show the typical distribution (Scheme 4). The branched methylpentenes t-4-MP-2 and 2-MP-2 (could also be isomerized from 2-MP-1, but 2-MP-1 was not detected) are the main products, with 4-MP-1, c-4-MP-2, t-2-Hex and c-2-Hex as byproducts. All these dimers are formed by an initial 2,1-insertion (Scheme 1). Double and mono branched isomers are mainly

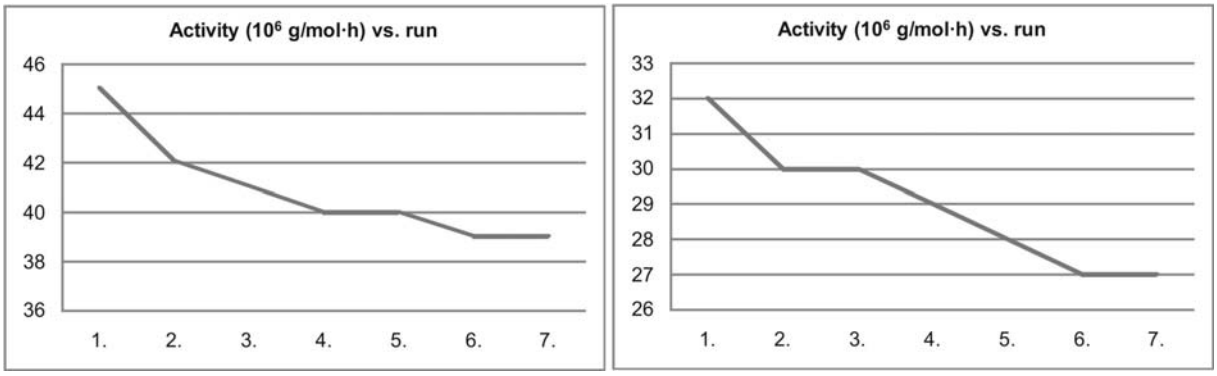
produced by a first 2,1-insertion. The second step makes the difference. High octane hydrocarbons (such as DMBs) are formed by a following 1,2-insertion. The main products of our work follow a 2,1-insertion. This hexene distribution is typical for the lewis acidic system containing nickel and $EtAlCl_2$. In none of these experiments, the desired highly branched dimers DMB-1 and DMB-2 were produced. High acidity favours the formation of less branched products and with this, less formation of double branched hexenes.[13]



Scheme 9. Part of gas chromatograph spectra with the typical product distribution of nickel catalyzed propylene dimerization.

Because of these promising results, the catalytic lifetime was investigated. For these reactions, the pressure Schlenk tubes were opened after a reaction time of one hour and the gas phase was evaporated (i.e. educts are separated from reaction products). The weight increase of the pressure Schlenk was determined. The reaction products were removed under vacuum, the Schlenk tube was refilled with propylene and a new run was started. A constant amount of catalyst and cocatalyst (Ni:Al = 1:1000) was kept for all the reruns (amount of cocatalyst = 0.9 mmol). The decrease of the catalytic activity can be caused partly by small amounts of impurities and the handling during the evaporation and refilling process. Scheme 5 shows a very good catalyst´s lifetime over the period of 7 runs. The activities of run 7 (i.e. after 7 hours) are still 87% (**1**) and 84% (**2**) of the starting activities. In these tests, the activities from Scheme 3 (which shows an average activity over 4 experiments per concentration) could not be reached. The selectivities for dimer products shrank from 85% to 74% (**1**) from the first to the seventh run respectively from 80% to 71% (**2**). All dimerization reactions showed the same distribution within the dimerization products (Scheme 4). These lifetime experiments of the catalyst show the enormous potential

of this system. The addition of the single TONs leads to the overall TON of 3.5 million (**1**) respectively 2.6 million (**2**). It is obvious that the system is still active at the end of the seventh run, so further experiments could be performed.



Scheme 10. Catalyst lifetime; Catalyst activity per rerun of complex 1 (left) and 2 (right).

Compared to the Dimersol system (which is an industrial process), the selectivity towards dimeric products is in all experiments higher. With up to 94% for C_6, the use of a controlling and bulky ligand improves the results from the Dimersol system (80% for C_6). An amount of 91% for methylpentenes inside the dimers and less amount of non branched hexenes (9%) shows the higher efficiency compared to the 72% (methylpentenes) of the literature, which is an important applied industrial process.[17-20] Lejeune and coworkers reported a chelated nickel phosphine based system with very high activities (factor 4 higher), which is one of the most fastest dimerization systems reported to date.[16] However, the use of 19800 equiv. MAO is extremely high.

In conclusion, we reported a highly active and selective system, that can be compared to established and reported homogeneous processes or systems.

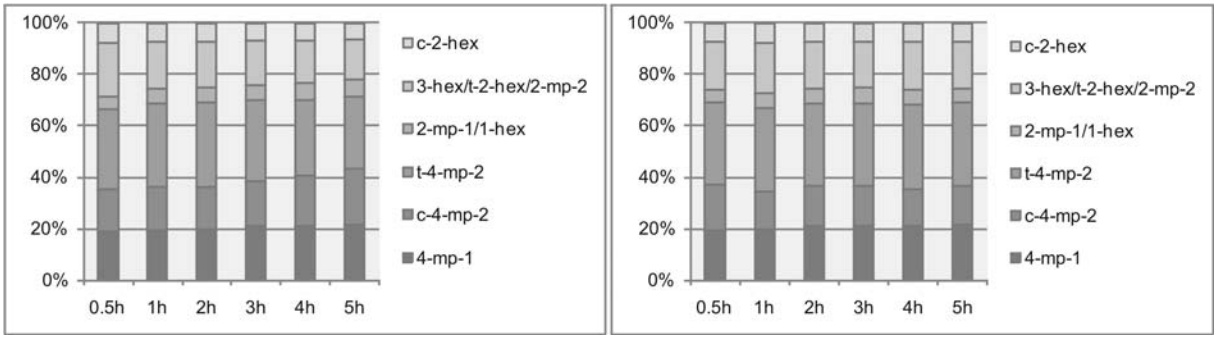
5.2.2. Heterogeneous dimerization reactions with propylene

The immobilization of metal complexes is an attractive goal in order to combine the advantages of homogeneous and heterogeneous catalysis.[27] The product isolation in a homogeneous system can cause a loss of the activity and the catalyst. In a heterogeneous system the product separation is quite elegant.[22] Herein we report the application of the two nickel phosphine complexes **1** and **2** in a fixed bed reactor.

Before carrying out the dimerization experiments, the support material required to be functionalized. With $EtAlCl_2$ on silica being an excellent oligomerization catalyst, the combination of cocatalyst and support material should be prevent. For this purpose, silica was impregnated with $AlEt_3$ solution to cap all free silanol groups, until no more gas evolution occurred.

The heterogeneous catalysts were prepared by the “incipient wetness” method and transferred under argon into the reactor tube. This was connected with the pipe system of the fixed bed reactor. The total reaction volume of the tube was 60 ml.

In contrast to homogeneous reactions in a closed system, the heterogeneous open system is fitted with a continuous flow of the reaction media. This results in shorter contact times between catalyst and olefin and has a tremendous effect on the product selectivity. According to 2.1 (the higher the activity the lower the selectivity) an excess of educts leads to higher selectivities towards dimer products. In both experiments the amounts of dimer products were constantly 100%. As shown in Scheme 6, the product distribution was nearly constant over the period of 5 hours. Only complex **1** showed slight changes in the percentage of cis- and trans-4-MP-2. These results underline the potential of the nickel phosphine system under homogeneous and heterogeneous conditions.



Scheme 11. Products distribution of the heterogeneous experiments with 1 (left) and 2 (right).

5.2.3. Homogeneous dimerization reactions with 1-butene

All dimerization experiments with 1-butene were performed under the “standard propylene conditions”. The change from propylene to butene reflects in a loss of activity. With one more carbon in the educt olefin, the activity shrinks by the factor 7. With average values of $7.3 \cdot 10^6$ and $5.2 \cdot 10^6$ g(dimer)/mol(cat.)·h, the system showed

still very high activities (table 4) (TON = 35,000 – 63,000). As observed for the experiments with propylene, complex **1** was more active than complex **2**. The selectivity values with 65% respectively 71% are lower than in the experiments with propylene. According to GC-MS spectra, 82% of the produced dimers are linear, which is in contrast to the catalytic propylene dimerization. Linear olefins need a 1,2-insertion as initial step. The main products 4-MP-1, c-4-MP-2 and t-4-MP-2 (all together 64%) from the dimerization of propylene are created by initial 2,1-insertion (Scheme 1), while 2-MP-2 can be isomerized from both insertion steps (but the loss of 2-MP-1 indicates 2-MP-2 as an isomerization product of 4-MP-1, c-4-MP-2 and t-4-MP-2). Dimerization of propylene mainly takes part by initial 2,1-insertion. This indicates a different behavior of the catalyst towards propylene respectively butene and could be caused by the steric difference of these olefins in the various catalytic steps.

The distribution of oligomers by carbon number shows a sharp Schultz-Flory distribution.

Table 3. Results for the dimerization of 1-butene under “standard propylene” conditions. The percentages were determined by relative area integration for each of the oligomers by carbon number from the GC-MS. The relative abundance peaks are derived from the total ion count for the peaks.

Complex	selectivity C_8 [%]	activity $\cdot 10^6$ g/mol·h	carbon distribution [%]		
1	65	7.3	20 [C_{12}]	11 [C_{16}]	4 [C_{20}]
2	71	5.2	17 [C_{12}]	7 [C_{16}]	5 [C_{20}]

Wasserscheid et al. reported a fluorinated acetylacetonate nickel system in buffered ionic liquids, that dimerizes 1-butene with a 68% selectivity for linear dimer products.[28] The use of an ionic liquid resulted in an enhancement of the activity, combined with a retention of selectivity and linearity in contrast to the original system with 85% dimer selectivity and 75% linear product selectivity.[29] Small and coworkers used a variety of catalysts based on cobalt, iron, vanadium and nickel for the dimerization of 1-butene. Nickel catalysts when activated with MAO or Et_2AlCl showed medium selectivities towards the formation of linear products within the dimeric phase of 55-62%. These nickel phosphine catalysts can make dimers with 72-84% selectivity. Compared to these literature known results, **1** and **2** reached the high dimer selectivities with 65 and 71%. However, the selectivity to linear dimers in

the dimer fraction of 82% is higher than reported for nickel catalysts, which are generally less selective than iron or cobalt based catalysts.[30] Indeed, the use of two-phase catalytic systems solve the problems of product separation.[31]

5.3. Summary and Conclusion

In the present work we report the results of dimerization reactions of propylene and 1-butene under different conditions with two nickel-phosphine catalysts. Both complexes showed a strong dependency from the activation ratio for the dimerization of propylene, whereby 1000 equiv. $EtAlCl_2$ yields in the highest activities of $52 \cdot 10^6$ g(dimer)/mol·h for complex **1**. The selectivity towards dimer products is indirect proportional to the catalytic activity. Lower activities of $13 \cdot 10^6$ g(dimer)/mol·h showed the highest selectivity of 94% towards hexene isomers. The use of a fixed bed reactor increased the catalytic selectivity up to 100%. Both homogeneous and heterogeneous conditions showed the same product distribution within the hexene isomers. The mono branched methylpentenes t-4-MP-2 and 2-MP-2 occurred as main products. With all products being in the range of the desired high octane number hydrocarbons, this nickel phosphine system showed an excellent performance for this application. While highly branched 1-butene dimers have the highest octane number, 18% of the produced octene isomers are branched, but produces linear dimers with a selectivity of 82%. Several characteristics as activity, selectivity, long term stability and the ability for hetereogenization makes the catalysts attractive catalysts for dimerization reactions.

5.4. Experimental Section

5.4.1. General considerations

Air- and moisture sensitive reactions were carried out under an atmosphere of purified argon using conventional Schlenk or glove box techniques. The dimerization reactions were performed with pressure Schlenk tubes.

The products of the dimerization experiments were characterized by a gas chromatograph (Agilent 6890) and GC/MS (FOCUS DSQ™ Thermo Scientific). The

samples were prepared under argon atmosphere. Mass spectra were recorded on a Varian MAT CH7 instrument (direct inlet system, electron impact ionization 70eV). Elemental analyses were performed with a VarioEl III CHN instrument. Acetanilide was used as standard.

5.4.2. Materials

All solvents were purchased as technical grade and purified by distillation over Na/K alloy under an argon atmosphere. All other chemicals were purchased commercially from Aldrich or Acros or were synthesized according to literature procedures. The ethylaluminumdichloride solution ($EtAlCl_2$, 0.9 M in heptane) was obtained from Acros. Kieselgel 60 (70-230 mesh, 60Å) from Macherey-Nagel was used as support material.

5.4.3. Homogeneous dimerization of propylene and butene

The respective complex was dissolved in toluene and activated with $EtAlCl_2$ solution (Ni:Al = 1:500-2000) and transferred into a 400 ml pressure Schlenk tube. The pressure Schlenk tube was filled with 50 ml liquid propylene / 1-butene and closed, warmed to room temperature with an external water bath and stirred. After the reaction time of 1 h, the Schlenk tube was opened and the solution was analyzed by GC / GC-MS

5.4.4. Heterogeneous dimerization experiments

Silica was prepared with Et_3Al solution. For this, 100 g of silica were stirred with 100 ml (1M Et_3Al solution) until no gas bubbles occurred. The prepared silica was washed with toluene and pentene and dried in vacuo.

For the heterogeneous reactions, the coordination compound was dissolved in an appropriate amount of toluene and activated with $EtAlCl_2$ in the ratio of Ni:Al = 1:1000. 14 g prepared silica were added to the solution and stirred for one hour. After evaporation to dryness the loaded silica was washed with pentane and evaporated to dryness. The heterogeneous catalyst was fixed in the reactor tube between glass wool. After connecting the reactor tube with the pipe system of the fixed bed reactor,

the tube was flowed with a propylene/pentane mixture (20 wt % propylene). The products were collected and analyzed hourly by gas chromatography.
The dimerization experiments were performed under standard conditions, e.g. room temperature, 80:20 pentane:propylene (wt%), 1.5 ml/min (flowrate), 24 bar reaction pressure and reaction time 5h. The content of complex on the support was 0.02 wt %.

5.5. Acknowledgement

We gratefully acknowledge financial support from ConocoPhillips, Bartlesville, USA.

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6. Practical heterogeneous complexes and their application as magnetically separable olefin dimerization catalysts

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Abstract:

We report the covalent support of functionalized nickel complexes on magnetic core-shell nanoparticles. Two ways of connecting the particle with the complexes were carried out. The first approach used the elegant hydrosilylation method between the alkene substituted nickel-complex and a silane. In a second approach, the particles were connected with the complexes via click chemistry (Huisgen 1,3-dipolar cycloaddition). For this purpose the nickel complexes were substituted with an alkyne moiety. Both complex types were used for the catalytic conversion of ethylene or propylene after activation with MAO. The characterization methods transmission and scanning electron microscopy, energy dispersive X-ray diffraction, and FT-IR spectroscopy were employed to characterize the successful heterogenization of the nickel complexes.

Keywords: core / shell materials, iron oxide, silica, phenoxyimin, nickel

6.1. Introduction

Magnetic nanoparticles have received a great deal of attention because of their potential use in biomedical applications, magnetic separation media and other high-functional devices.[1-3] A spherical nanoparticle with a core–shell architecture is a viable way to combine multiple functionalities on a nanoscopic length scale.[4]

Homogeneous catalysis suffers from the problematic separation of the catalysts and products, and the re-use of the catalyst. These problems are of environmental and economic interest in large-scales syntheses. A possible heterogenization of the existing catalysts could be an attractive solution to this problem.

The pioneers of magnetic chemistry are superparamagnetic iron oxid particles, such as magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3). Besides these oxide materials, pure metal magnets made out of iron or cobalt are produceable in relevant scales.[5-8] Both blank particles are vulnerable to lose magnetism. For further applications, the particles need to be protected / stabilized against chemical, thermal or mechanical influences. In general, there are three ways of stabilization: 1) addition of monomers such as carboxylates or phosphates,[9-12] 2) coating with inorganic materials such as silica or gold metal,[13-18] 3) coating with organic matrices, as surfactants and polymers.[19-24]

Silica plays an important role in the preparation of core–shell nanoparticle systems due to its excellent physical and chemical properties: it is optically transparent, easily functionalized, and the simple and robust synthesis of silica particles from the monomer tetraethoxysilane (TEOS) has been established for many decades, most frequently following the Stöber procedure.[4,25] The silica-coated Fe_2O_3 magnetic nanoparticles (MNPs) could combine the advantages of magnetic cores and functionalizeable silica surfaces. While classic heterogeneous catalysts are widely used in industry, lower activities compared to homogeneous systems are commonly detected.[24] A great proportion of these catalysts is deep inside the supporting material and thus reactants have limited access to the catalytic sites.[26] Decreasing the size of the support down to the nanometer scale, the surface area is increased and the support can be evenly dispersed in solution, forming a homogeneous emulsion.[10]

In recent years, much attention has been focused on catalysis research and magnetic nanoparticles have been employed in important reactions as hydrogenation, hydroformylation, Suzuki-Miyaura and Heck couplings, and olefin metathesis.[27-29]

Herein we report the application of nickel complexes supported on magnetic nanoparticles during the catalyzed polymerization and dimerization of ethylene respectively propylene.

6.2. Results and Discussion

In the following section, we describe in detail the characterization and catalytic behavior of the synthesized catalysts on magnetic nanoparticles. These core-shell particles contain a Fe_2O_3 core coated with a silica layer. The silica shell has plenty of hydroxyl groups for potential derivatization on which the catalysts can be successfully immobilized. The series of catalysts were designed to include two ways of linkage with the support. Both methods contain simple reaction steps and uncomplicated handling and anchoring of a triethoxysilan group. The first approach uses the elegant hydrosilylation method to combine the bis(imin)nickel complex with the support material. The second approach describes the combination of the magnetic particles and the alkyne end-functionalized phenoxyimine-nickel complexes using the Huisgen 1,3-dipolar cycloaddition.[30,31] For both approaches, the same magnetic core-shell particles containing a Fe_2O_3 core coated with a silica layer were used. TEM images in Figure 1 (left side) show the Fe_2O_3 cores with an average diameter of 12 nm. A thin ~16 nm layer of silica was coated on this core, via a sol-gel process to give silica-coated Fe_2O_3 magnetic nanoparticles with an average diameter of 45 nm (Figure 1, right side). The idea was to create a heterogeneous catalyst for facile product separation for the catalytic conversion of olefins.

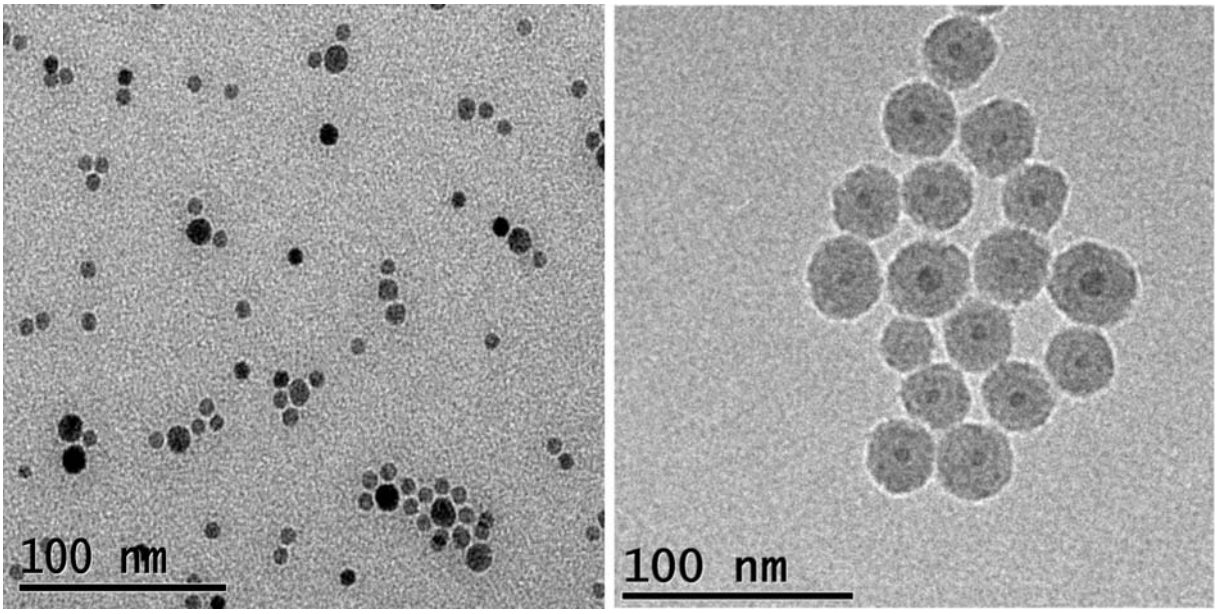


Figure 1. TEM images of the iron oxide cores (left side) and the magnetic nanoparticles with silica shell (right side).

As shown in Figure 2, an external magnet can remove the magnetic particles out of the solution, or generate two phases for following product separation.

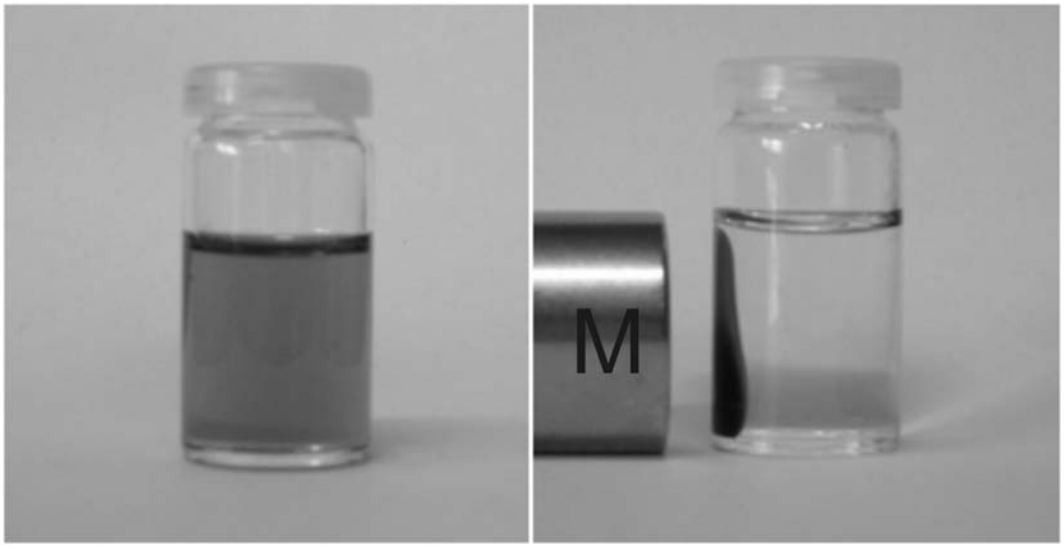
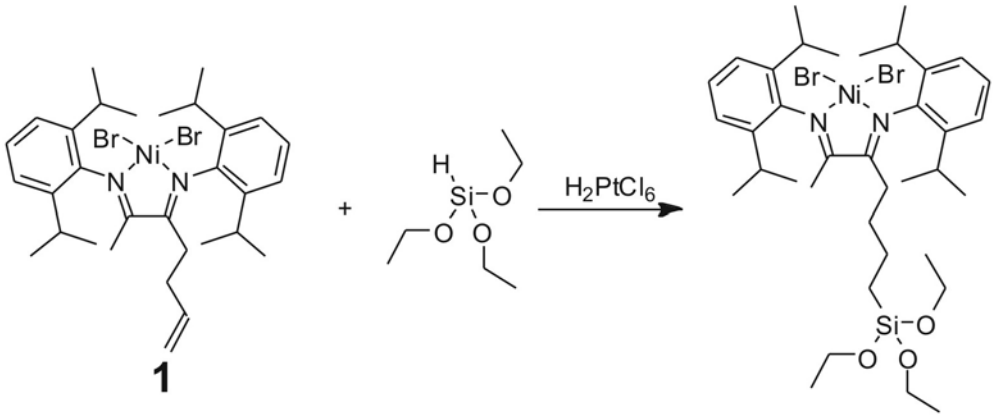


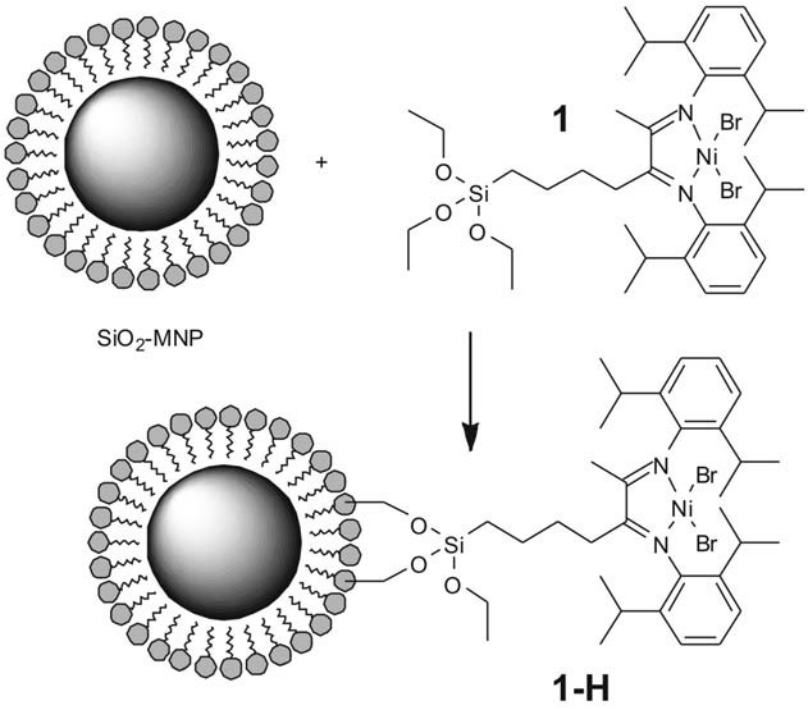
Figure 2. Left side: Dispersed magnetic nanoparticles. Right side: Particles can be separated via a strong magnet (M).

Approach 1:

The plan of synthesis involves a precursor consisting of an ω-alkenyl diimine moiety coordinated to nickel(II)bromide and a silane that can react with the silica particles. After the silane-ene reaction (Scheme 1) the complex with the triethoxysilan moiety can be coupled directly with the support material (Scheme 2). This hydrosilylation reaction is quick and elegant. Complex **1** was prepared according to the literature.[32]



Scheme 12. Hydrosilylation reaction of the diimine nickel complex and triethoxysilane.



Scheme 13. Route of heterogenization for complex **1**.

After heating in toluene, the complex is immobilized (**1-H**) covalently on the silica support. Following the product removal by centrifugation, the particles were washed with toluene, THF and DCM.

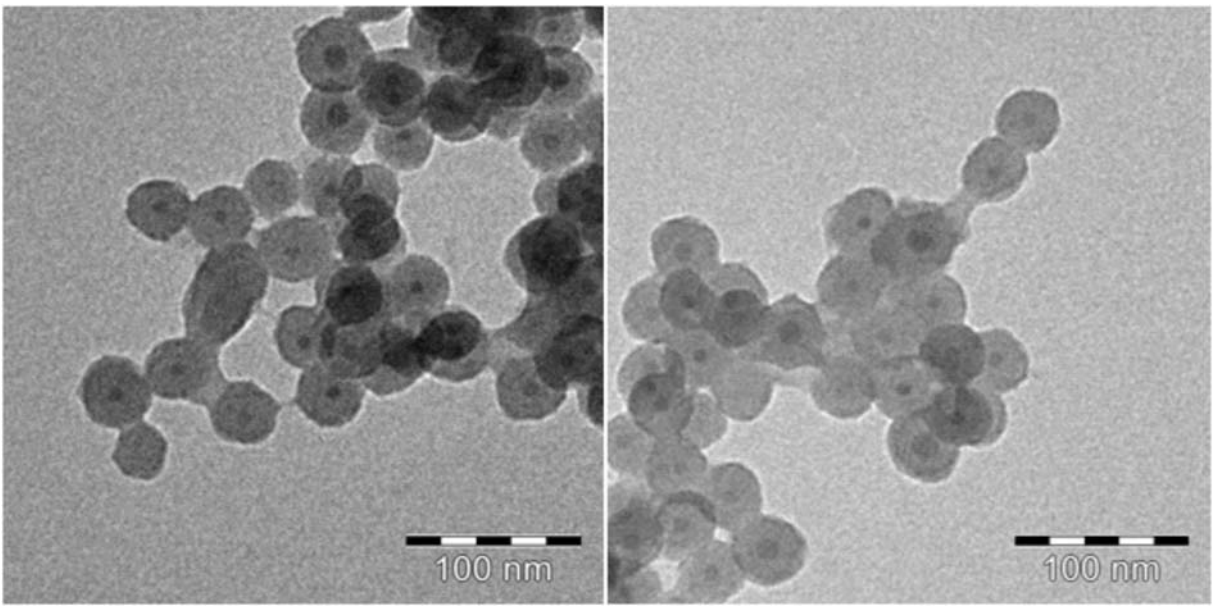


Figure 3. TEM image of **1-H**, The surface is distinctly coarser compared to the blank particles.

TEM images in Figure 2 show the core-shell structure with the modified surface of the particles. The surface of the particles with connected complexes is distinctly coarser

than the blank Fe_2O_3-SiO_2-MNPs. It is obvious that a thin layer of supported catalyst is surrounding the silica particles. EDX was used to identify the chemical composition at the surface and of the particles. The EDX spectra in Figure 4 clearly shows typical peaks. A small peak from the iron core is obvious. Silicon (shell) and oxygen (core and shell) are the dominant peaks. The typical nickel and bromine peaks can be confirmed by peak integration and show a 4.2% to 7.9% ratio which represents an atomic ratio of 1:1.9 which confirms the composition $NiBr_2$. These results are in good agreement with the proposed structure and the conclusion withdrawn from the TEM image.

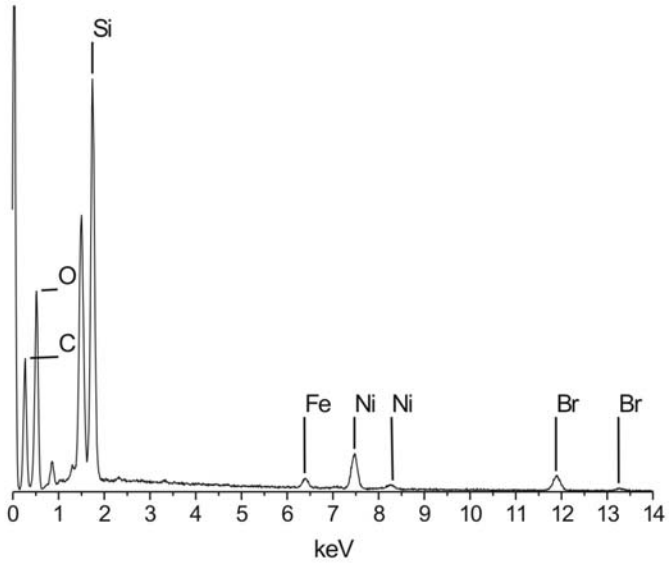
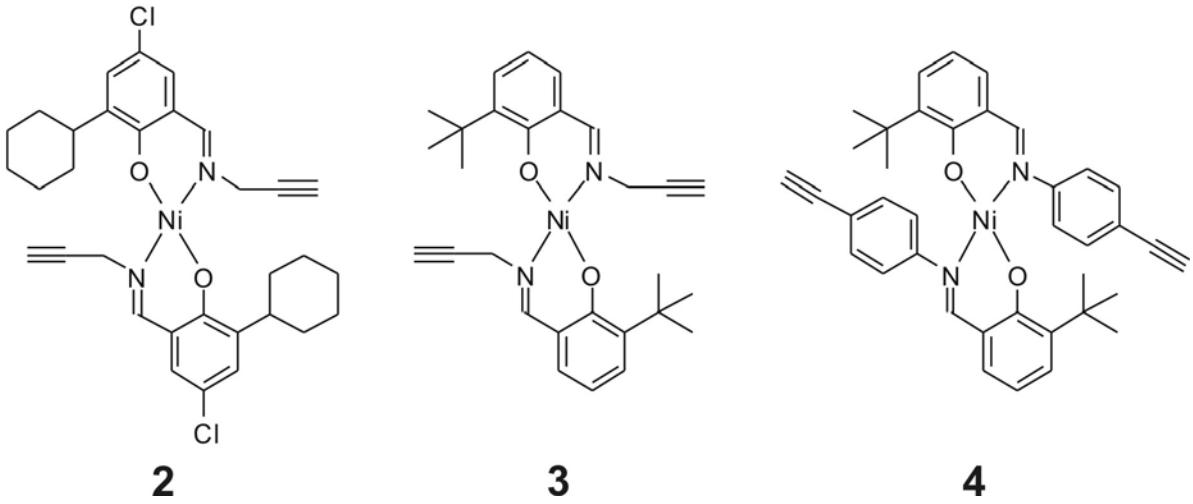


Figure 4. EDX spectra of the heterogeneous complex **1-H**.

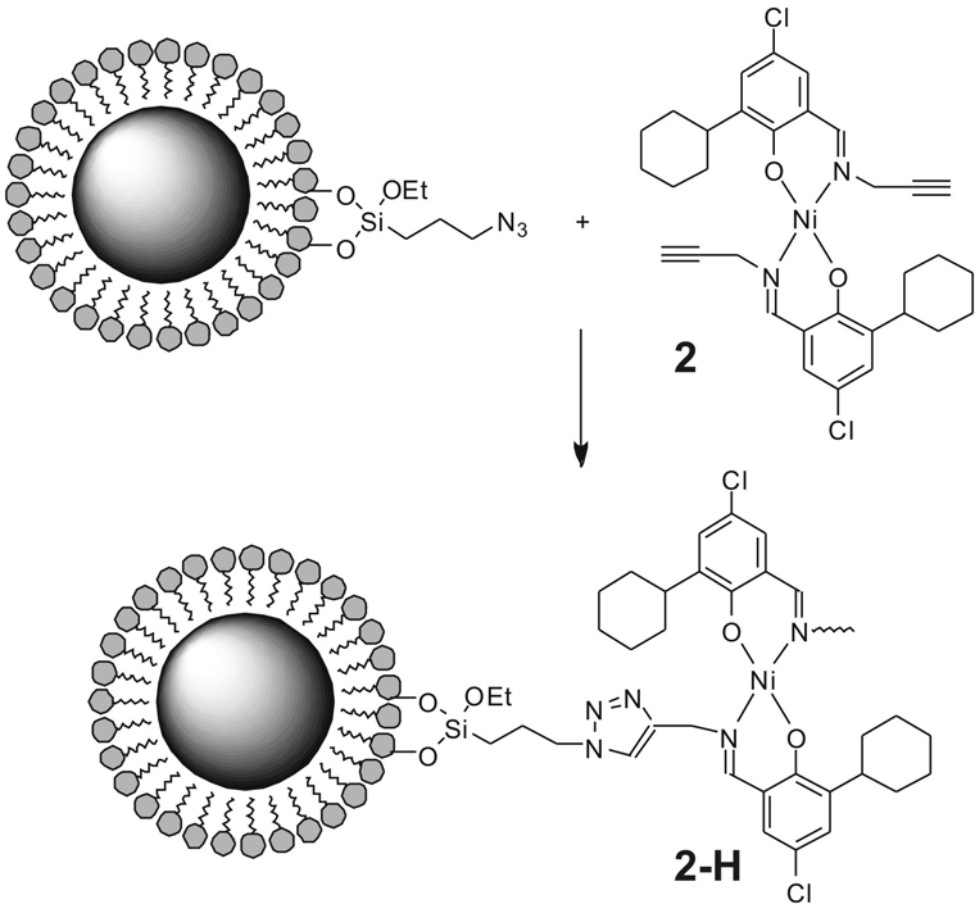
Approach 2:

In the second part we discuss the heterogenization of phenoxyimine nickel complexes. Here, the Huisgen 1,3-dipolar cycloaddition is used to attach azido functionalized Fe_2O_3-SiO_2-MNPs with the alkyne group of the complex.

This way is a very adaptable and orthogonal method to attach any compound carrying an alkyne group to a desired surface. Therefore, three different nickel complexes bearing an alkyne group were synthesized and connected with the support. The respective ligands were synthesized according to the literature[33] and the complexes were obtained via a known process.[34]



Scheme 3. Prepared complexes **2-4** containing an alkyne moiety.



Scheme 4. Route of heterogenization for complexes **2-4**.

Figure 5 shows the FT-IR spectra of the pure Fe_2O_3-SiO_2-MNPs, the nickel-phenoxyimine connected Fe_2O_3-SiO_2-MNPs (**2-H**) and the pure complex **2**. The silica surface is characterized by two dominant peaks. The nonbonded surface Si-OH

groups with the band in the range of 3300-3700 cm^{-1} and the characteristic Si-O-Si vibration (1080 cm^{-1}).

The supported complex shows two peaks at 1620 and 1730 cm^{-1}, typical for the C=N and C=C stretching bands. The created triazole group shows a typical peak at 1450 cm^{-1}, dominated by the peaks of the support. This resonance is not very intense, but it is the only characteristic resonance of the triazole group and confirms a successful grafting. The phenoxyimine complex unit itself shows no strong IR stretching frequency and it is likely masked by the silica bands of the support.

The pure complex shows the very intense band of the C-H vibration of the alkyne group (3280 cm^{-1}), and the C≡C vibration at 2120 cm^{-1}.

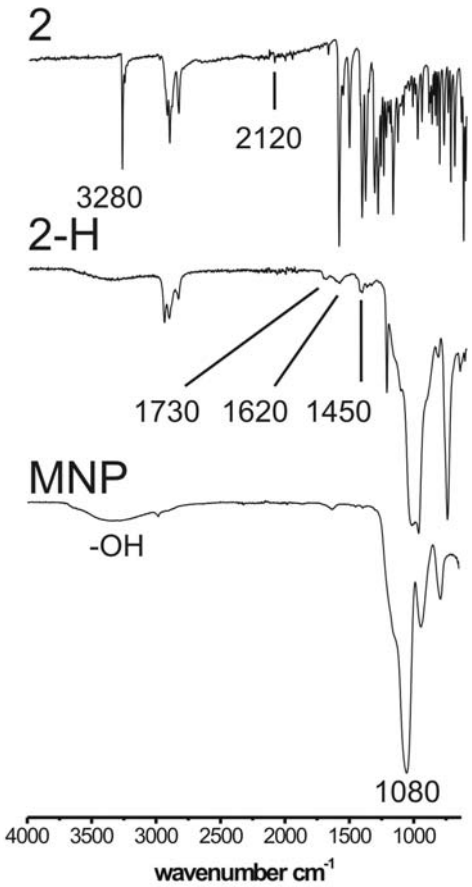


Figure 5. FT-IR spectra of the pure nanoparticles (MNP), the supported complex (**2-H**), and the corresponding pure complex (**2**).

After the click-reaction with the alkyne-complexes, the particles were observed by TEM. The image of Figure 6 shows the core-shell structure with the modified surface of the particles. The surface of the heterogeneous complexes is distinctly coarser

than the blank Fe_2O_3-SiO_2-MNPs. All these aspects indicate that the heterogenization reaction was successful and the IR-results are confirmed.

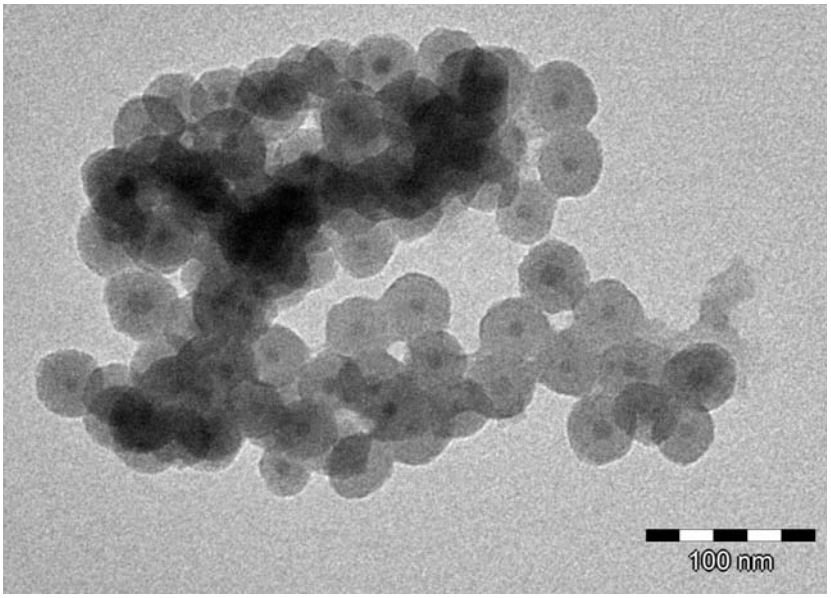


Figure 6. TEM image of **2-H**, The surface is distinctly coarser compared to the blank particles

Catalytic properties:

The catalytic performance of the heterogeneous catalysts **1-H**, **2-H**, **3-H** and **4-H** is described in the following section.

The bisimino-nickel complex **1-H** was applied as catalyst for the catalytic polymerization of ethylene. Recent works described the homogeneous polymerization of ethylene with bisimino-nickel complexes after activation with MAO.[32] In our experiments, the immobilized catalyst was stirred in toluene, and ethylene was added under small pressure for 20 minutes to the solution. After quenching with isopropanol, the polymer particles were washed and separated via centrifugation. The particles were visualized by SEM in Figure 7. The images clearly show spherical particles with a rough polymer surface. Different particles sizes from 0.1 to 1.5 µm were observed. The images show that polymerization happens at the catalysts on the particle surface and that particles grow independent. Unfortunately a broad polymer particle size distribution was observed.

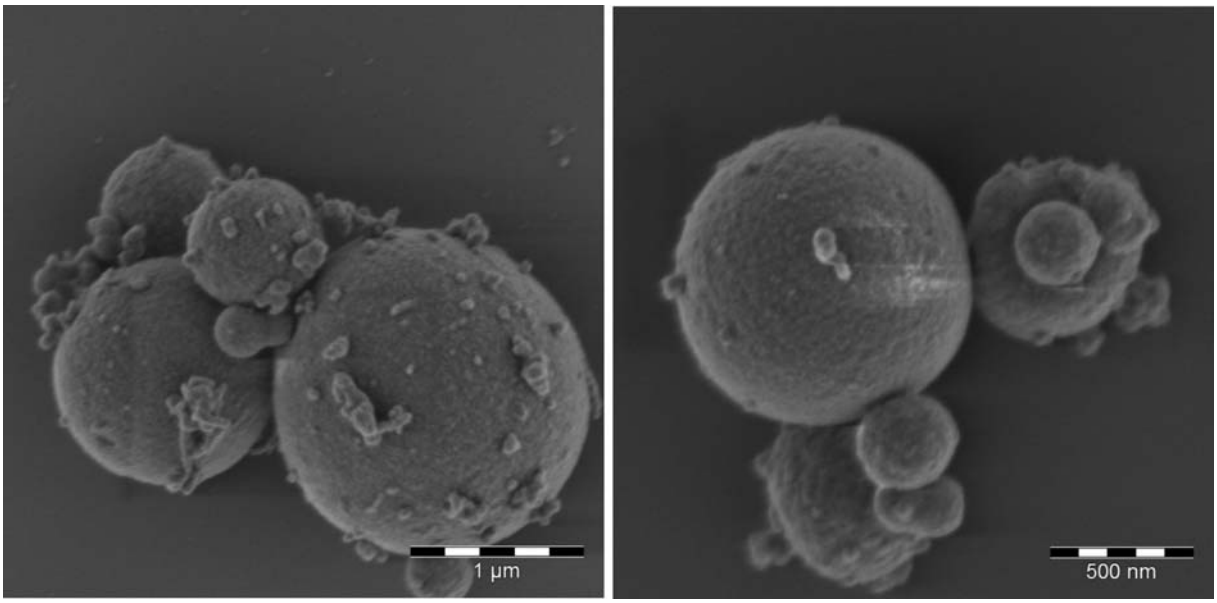
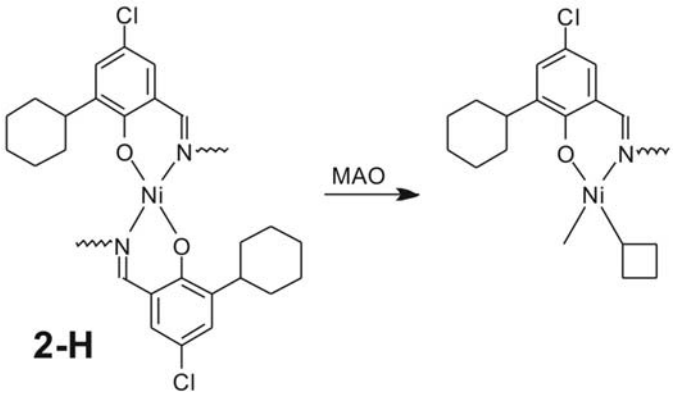


Figure 7. SEM image of the polyethylene particles polymerized by **1-H**.

These polymerization tests prove that covalently immobilized complexes on SiO_2MNPs are catalytically active and that catalysis happens at these functionalized particles. The polymerization experiments were carried out as control experiments for the following dimerization experiments, where no change in the shape and size of the catalytic active particles can be observed.

During the catalytic test, we mainly focused on the role of the support in order to ease the product separation. Thus, all catalytic tests have been carried out using a heterogeneous catalyst in a closed system (pressure Schlenk tube). Herein, we report the use of phenoxyimine-nickel complexes, which are normally high active for the dimerization of propylene after activation with MAO.



Scheme 5. Phenoxyimine nickel complexes before and after activation with MAO. The square represents the free coordination site.[35]

With two ligands coordinating the central metal, the phenoxyimine complexes have two sides for heterogenization (Scheme 5). After activation with MAO, one ligand leaves the complex and leaves a free coordination side. After activation, a single complex is fixed on a single side to a particle. With all three immobilized catalysts the catalytic dimerization of propylene was performed.

While bisimine nickel catalysts are known for their catalytic polymerization of ethylene,[32] phenoxyimine nickel complexes are highly active for the dimerization of propylene.[34]

Table 4. Results of the catalytic dimerization of propylene with the heterogeneous complexes **2-H**, **3-H** and **4-H**.

	C 6 [%]	C 9 [%]	C 12 [%]	Activity of the free catalyst [kg(product)/mol h]
2-H	75	25	-	264
3-H	92	6	2	405
4-H	87	7	6	380

The results in Table 1 show the dimerization reactions of the supported catalysts **2-H**, **3-H** and **4-H** after activation with MAO. All three heterogeneous catalysts show high selectivities of up to 92 % for dimeric products. Besides some trimeric products nearly no higher oligomers are formed. To compare the results of the supported catalysts, Table 1 shows the dimerization results of the free unsupported catalysts. The catalytic activities are in the range of 264 to 405 kg(product)/mol h which represents TONs of 3150 (**2**), 4520 (**4**) and 4820 (**3**). The gas chromatograms of the dimerization experiments show the typical distribution. The branched methylpentenes t-4-MP-2 and 2-MP-2 are the main products, with 4-MP-1, c-4-MP-2, t-2-Hex and c-2-Hex as byproducts.

All three heterogeneous catalysts are highly efficient for the catalytic dimerization of propylene. The catalytic activities and the product distribution are in a range according to the literature.[34]

The reaction products were decanted after separating the particles with a strong magnet.

6.3. Summary and Conclusion

We demonstrate the successful heterogenization of phenoxyimine nickel and bis(imine) nickel complexes via an azide-alkyne click-reaction and hydrosilylation reaction. Uniformly sized silica-coated magnetic nanoparticles were synthesized and used as support material. The complexes were covalently bonded to the silica shell, according to EDX, TEM and FT-IR observations. Polymerization of ethylene after activation with MAO was successful and SEM images clearly show spherical particles with a rough polymer surface. Dimerization reactions showed the excellent catalytic properties of the heterogenizated phenoxyimine nickel complexes. The compared use under homogeneous “free” conditions resulted in the same product distribution.
The facile preparation and the catalytic properties show the high potential of this heterogeneous system. Catalysts can be separated by the means of a strong magnet, and ease the problematic product separation. The application of this catalytic system combines homogeneous activities and selectivities, and the separation of the product and the catalyst phase in heterogeneous systems.

6.4. Experimental Section

6.4.1. General considerations

Air- and moisture sensitive reactions were carried out under an atmosphere of purified argon using conventional Schlenk or glove box techniques. The dimerization reactions were performed with pressure Schlenk tubes.
The products of the dimerization experiments were characterized with a gas chromatograph (Agilent 6890) and GC/MS (FOCUS DSQ^{TM} Thermo Scientific). Mass spectra were recorded on a Varian MAT CH7 instrument (direct inlet system, electron impact ionization 70eV). Elemental analyses were performed with a VarioEl III CHN instrument. Acetanilide was used as standard.
Bright-field Transmission electron microscopy (TEM) was performed on Zeiss CEM 902 and LEO 922 OMEGA electron microscopes operated at 80 kV and 200 kV, respectively. Data evaluation and processing was carried out with Soft Imaging Viewer and Image Tool.

Scanning electron microscopy (SEM) was performed using a LEO 1530 Gemini instrument equipped with a field emission cathode with a lateral resolution of approximately 2 nm. The acceleration voltage was chosen between 0.5 kV and 30 kV for EDX.
Energy Dispersive X-Ray Scattering (EDX) spectra were measured with a LEO 1530 Gemini instrument using an Oxford EDX INCA 400 device. The obtained spectra were analysed with the microscope software and the present elements in the sample were detected by their corresponding X-ray absorption peaks. For the measurements a small amount of the sample was prepared onto a cleaned silicon waver and was sputtered with carbon to make the sample surface conductive.
Fourier Transform Infrared (FT-IR) spectras were recorded on a Perkin Elmer FT-IR Spectrometer (Spektrum One).

6.4.2. Materials

All solvents were purchased as technical grade and purified by distillation over Na/K alloy under an argon atmosphere. Iron(0)pentacarbonyl ($Fe(CO)_5$; 99.9 %), oleic acid (90 %), dioctyl ether (> 99%), polyoxyethylene(5)nonylphenylether (Igepal ® CO 520), 3-(trimethoxysilyl)propyl methacrylate (MPS; > 98 %) ammonium hydroxide (NH_4OH; 28 % in H_2O), tetraethylorthosilicate (TEOS; > 98 %), were purchased from Sigma Aldrich. All other chemicals were purchased commercially from Aldrich or Acros or were synthesized according to literature procedures. The methylaluminoxane solution (MAO, 30wt.% in toluene) was obtained from Albemarle, USA.

6.4.3. General procedure for the synthesis of γ-Fe_2O_3 nanoparticles

The synthesis of γ-Fe_2O_3 nanoparticles was adopted by the publication of Hyeon et al.[36] A 250 ml two-neck round-bottom flask, connected to a reflux condenser, was charged with 120 ml dioctyl ether and 29.0 ml oleic acid (25.76 g, 91.2 mmol) and degassed with N_2 for 15 min. The reaction mixture was heated to 100 °C under N_2 atmosphere before adding 4ml $Fe(CO)_5$ (30.4 mmol). Subsequently, the resulting mixture was heated to reflux and kept for 1.5 h until the solution colour turned to black. After cooling down to room temperature the reaction mixture was stirred under

air to initiate the oxidation process of iron to achieve γ-Fe_2O_3 nanoparticles. The yielded particles were precipitated with ethanol and separated by means of a NbFeB-magnet. The particles were immediately redispersed in toluene, THF or *n*-hexane. For further purification the precipitation and separation process was repeated. To yield smaller-sized iron oxide particles 9.7 ml (8.58 g, 30.4 mmol) of oleic acid were used.

6.4.4. General procedure for the synthesis of Fe_2O_3/SiO_2 core shell particles

The synthesis is based on the experimental procedure published by Ying et al.[37] Polyoxyethylene(5)nonylphenyl ether (0.23 g, 0.54 mmol, Igepal CO-520) was dispersed in a small flask containing 4.5 ml cyclohexane by sonication. Next, 400 µl of γ-Fe_2O_3 nanoparticles dispersed in cyclohexane (0.5 mg/ml) were added to the flask. The resulting mixture was vortexed until the mixture became transparent. Ammonium hydroxide (29.4%, 40 µl) was added to form a transparent, slightly brown reverse microemulsion. Finally, tetraethylorthosilicate (30 µl, TEOS) was added, and gently vortexed. The reaction was continued for ≤ 48 h at room temperature. The resulting Fe_2O_3/SiO_2 nanocomposite particles were precipitated by adding methanol, and collected by centrifuging. The collected Fe_2O_3/SiO_2 nanoparticles were redispersed in ethanol, and purified by sonication and centrifugation. The centrifugation and ethanol washes were repeated three times. The magnetic core shell particles could also be magnetically collected. The final product was redispersed in ethanol.

6.4.5. General procedure for the synthesis of the complexes

2, 3, 4: 10 mmol of the respective ligand precursor in 100 ml ethanol were mixed with 5 mmol $Ni(OAc)_2$ * x H_2O. The solution was stirred under reflux for 24 h. The volume was reduced and the complexes precipitated by the addition of pentane. The products were filtered through a glas frit and washed with pentane. The complexes were obtained as green solids with yields in the range of 73 – 82%.

2: MS data: 608 ($M^{\bullet+}$) (68), 357 (9), 333 (72), 236 (100). $C_{32}H_{34}Cl_2N_2O_2Ni$: calcd. C 63.19, H 5.63, N 4.61. Found C 63.08 H 5.52 N 4.53%.

3: MS data: 485 ($M^{\bullet+}$) (37), 214 (100). $C_{28}H_{31}N_2O_2Ni$: calcd. C 69.16, H 6.43, N 5.76. Found C 69.64.08 H 6.31 N 5.47%.
4: MS data: 610 ($M^{\bullet+}$) (41), 510 (41), 335 (27), 276 (100). $C_{38}H_{36}N_2O_2Ni$: calcd. C 74.65, H5.93, N 4.58. Found C 74.17, H 5.34, N 4.81%.

6.4.6. Synthesis of the supported complexes

1-H An amount of 630 mg (1.28 mmol) of the complex was dissolved in a minimum amount of toluene. 5 mg (12 µmol) of Speier´s catalyst (H_2PtCl_6) was added. Triethoxysilane (233 mg, 1.42 mmol) was added dropwise over a period of 30 minutes. After 24 hours of stirring, the complex precipitated by the addition of pentane. The solution was removed and 100 mg of the magnetic nanoparticles in 25 ml toluene were added. The suspension was stirred for 3 d at 85°C. The slight blue solution was separated from the brown-green solid and the particles were thoroughly washed with toluene, THF and DCM.

2-H, 3-H, 4-H: An amount of 8.8 g chloropropyl(triethoxy)silan and 2.4 g sodiumazid were stirred in 100 ml DMSO for 4 d. A white solid precipitated and was filtered off. 200 mg of the magnetic particles were added to third of the solution and stirred for 4 days at 80°C.
The particles were separated and suspended in toluene with an excess of the respective catalysts (1g). Copper chloride (2mg) and sodium ascorbate (4mg) were dissolved in 5 ml distilled water and added to the stirred mixture. After a reaction time of 4 days, the particles were separated via centrifugation and washed thoroughly with toluene, ethanol and pentane.

6.4.7. Polymerization of ethylene

An amount of 25 mg of the supported catalyst was placed in a pressure Schlenk tube with 10 ml toluene and 12 ml MAO solution (10%wt.). Ethylene was added under pressure (2 bar) for 20 min. at room temperature. The particles were carefully washed with isopropanol and toluene and separated from the solution and dried under vacuum.

6.4.8. Dimerization of propylene

An amount of 25 mg of the supported catalyst was placed in a 400 ml pressure Schlenk tube with 5 ml of toluene and activated with 10 ml MAO solution (Ni:Al = 1:500). The pressure Schlenk tube was filled with 50 ml liquid propylene and closed, warmed to room temperature with an external water bath and stirred. After the reaction time of 1 hour, the Schlenk tube was opened and the solution was analyzed by GC.

6.5. Acknowledgement

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7. Highly efficient olefin dimerization catalysts

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Abstract: We report the performance of the olefin dimerization catalysts $TiCl_4$*2THF, $CoCl_2$ and $NiBr_2$*DME in combination with MAO. The aim was to dimerize the olefins propylene, 1-butene, *cis*-butene, 1-pentene and 1-hexene very selectively and with high conversion rates. Different metal to ligand ratios gave different results. The conversion rates depended on the reaction times. The activation ratios had a strong influence on the conversions and activities. A special property of the catalysts makes our system smart; A color change indicates the deactivation of the catalyst by pollution on air. The luminescent and fluorescent properties of our systems change dramatically.

Keywords: Dimerization, Olefin, Catalyst, MAO, Selectivity

7.1. Introduction

Unsatured short chained hydrocarbons are low priced educts for polymerization, oligomerization and metathesis reactions, produced by unselective thermal cracking processes.[1] Especially the dimerization of propylene plays an important role for the formation of gasoline with a high octane number. As a result branched hexenes can be obtained and used as gasoline blending components. The Research Octane Number (RON) rises with the number of branching,[2-6] from RON = 96-99 for methylpentenes to 101 for dimethylbutene.[2, 7-8] Linear hexenes are in the range from 73-94 and play no role as additives for gasoline improvement. With the ban of lead-alkyl compounds and methyl-*tert*-butyl ether as anti knocking agents from gasoline, branched hydrocarbons represent a very important class of compounds for gasoline reformulation.[9]

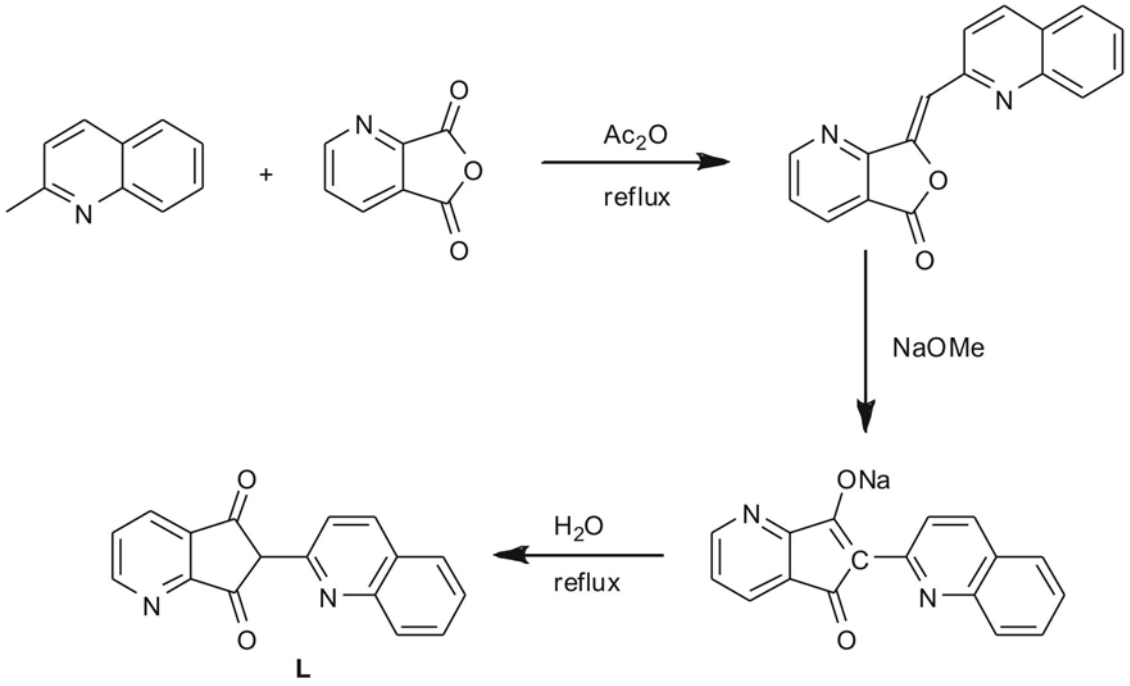
The Cetane Number (CN) gives a rate for the ability of ignition in diesel fuel engines. In general, the longer and more linear a hydrocarbon the higher the CN.[10] Because of the self ignition of diesel fuel in the compressed air of an engine (700-900°C), higher CN means lower combustion temperatures and this results in cleaner combustions and lower emissions. While 1-hexene has a CN of 27, the dimerization product 1-undecene has 65 and the trimerization product 1-octadecene has 71. For comparison, normal diesel has a CN higher than 51, ARAL Ultimate Diesel has higher than 60.[9,11] The dimerization of low boiling olefins is very interesting for the production of additives for gasoline fuel (dimerization of propylene and butenes) and addivites for diesel fuel (in the case of 1-pentene and 1-hexene).

The invention of highly active iron- and cobalt-based olefin polymerization catalysts in the late 1990s has led to high interest in the chemistry of transition metal complexes bearing tridentate bis(imino)pyridine ligands.[12–23] In the late 60s, Wilke described a catalyst system containing a π-allylnickel complex in combination with a tertiary phosphine and a Lewis acid like aluminum trichloride producing mainly propylene dimers (80-85%).[24] Reduction of nickel acetylacetonate with alkylaluminum chlorides resulted in higher activities compared to the Wilke system.[25]

To avoid the problems of product separation under homogeneous conditions, Chauvin and co-workers reported the dimerization of propylene in chloroaluminate ionic liquids.[26,27] The *Institut Francais du Pétrole* (IFP) recently established this biphasic system named Difasol for the dimerization of propylene with high selectivities.[28] Here we report the application of a catalytic system for the selective dimerization of olefins. The kind of metal center, the metal / ligand interaction and the activation ratio are of great interest. We call it a smart catalytic system, because the system gives alert when it starts to get deactivated.

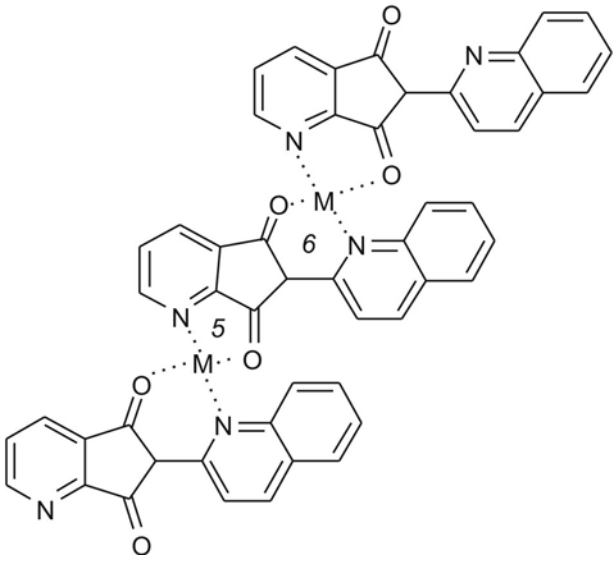
7.2. Results and Discussion

*7.2.1. Synthesis of the ligand precursor **L***



Scheme 14. Route of synthesis of the organic compound **L**.

The potential ligand **L** was synthesized via a simple synthetic route in three steps according to the literature (Scheme 1).[29] This simple availability and the temperature and air stability ease the handling during catalytic experiments. Compound **L** is very attractive for the coordination of transition metal salts. With two nitrogen and two oxygen atoms in one molecule, different coordination modes can be realized. These different coordination states can generate five or six membered coordination rings depending on the biting of the ligand (Scheme 2). With varying the ratio of metal to ligand, more structures with multiple coordination states and super lattices can be formed.



Scheme 15. Coordination modes; five and six membered rings and possible super lattices.

This versatile and flexible coordination behavior with diverse electronic and steric properties makes our system interesting for the catalytic dimerization of olefins.

7.2.2. Catalytic dimerization reactions

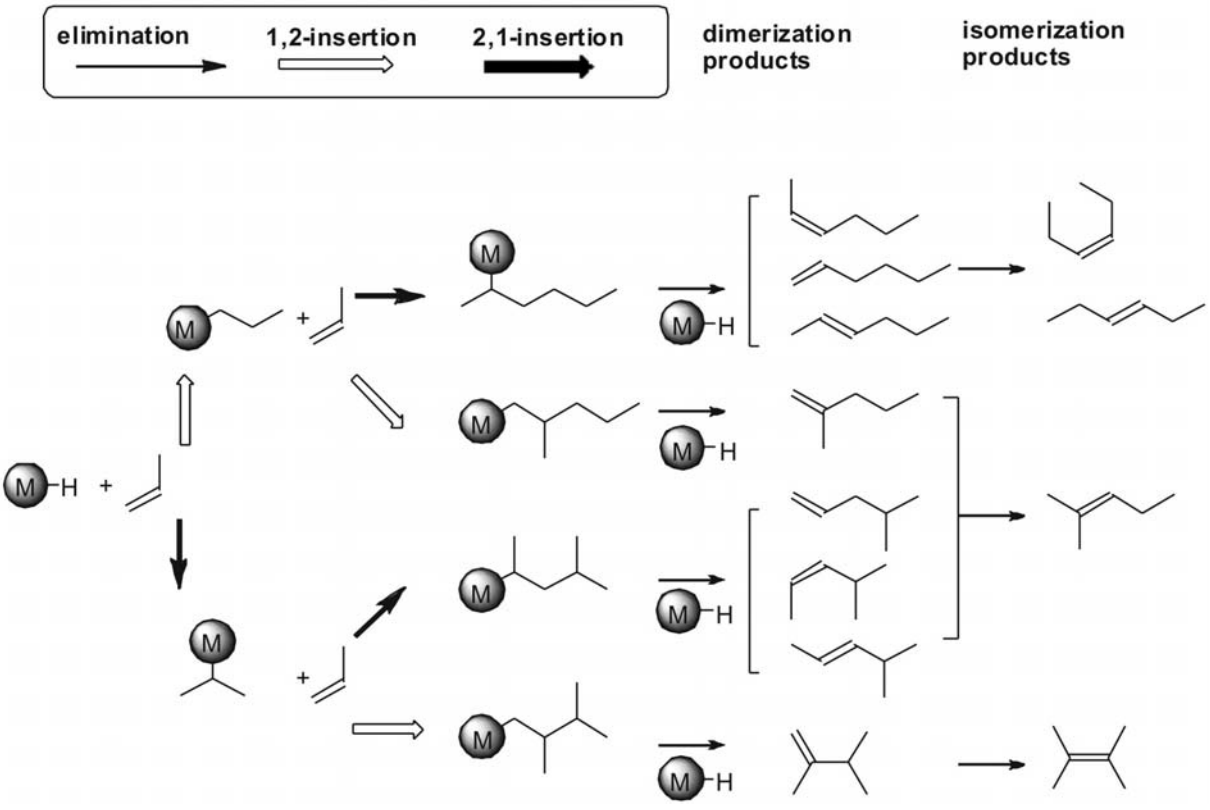
For the catalytic dimerization reactions of the olefins propylene, 1-butene, *cis*-butene, 1-pentene and 1-hexene, three different metal salts were combined with the organic compound **L** in different ratios and activated with MAO. Table 1 shows all used compositions and the respective abbreviations for three different metal salts with three different metal to ligand ratios with different activation ratios. The respective metal salt and the ligand precursor were combined and stirred until a color change occurred (ca. 1h). The cocatalyst was added and stirred for further 30 min. and the dimerization experiments were started after the addition of the olefin.

Table 1. Compositions and activation ratios of the respective catalytic dimerization experiments. A 1 M solution of MAO in toluene was used as cocatalyst, with varying activation ratios.

Abbreviation	Composition Ligand:metal ratio	Activation ratio MAO, Al:M	Used metal salt
A	L-M	1:500	$TiCl_4$*2THF
B	2L-M	1:500	$TiCl_4$*2THF
B-2	2L-M	1:1000	$TiCl_4$*2THF
C	L-2M	1:500	$TiCl_4$*2THF

D	LM	1:500	$CoCl_2$
E	2L-M	1:500	$CoCl_2$
E-2	2L-M	1:1000	$CoCl_2$
F	L-2M	1:500	$CoCl_2$
G	LM	1:500	$NiBr_2$*DME
H	2L-M	1:500	$NiBr_2$*DME
H-2	2L-M	1:1000	$NiBr_2$*DME
I	L-2M	1:500	$NiBr_2$*DME

Scheme 3 figures out all possible dimerization products of the catalytic dimerization of propylene. While dimerization is quite simple, higher oligomerization reactions are more complex. 12 hexene isomers can be obtained during dimerization (for propylene), a further reaction with a dimer (trimerization) makes this more complicated.



Scheme 16. Dimerization products of propylene and catalytic cycles.

Reactions of 1-pentene or 1-hexene can lead to up to 18 dimerization products. Because of these various isomers, we focused our work on the product selectivity (dimer, trimer, tetramer …) and catalytic activities/conversion.

7.2.2.1. Homogeneous dimerization reactions with propylene

The activity was determined by the weight increase of the reaction vessel after removing propylene. The nickel containing catalysts showed the highest activities of up to 420 kg(product)/mol(catalyst)/h (Table 2). All four experiments with nickel complexes showed higher activities than any other experiment. Only the catalytic system **E** reached quite high activities with 159 kg/mol/h. Titanium complexes showed the lowest activities in the range of 17-54 kg/mol/h. It is obvious that an increase of the activation ratio had a positive effect on the catalytic activity. All results (**B**, **B-2**; **E**, **E-2**; **H**, **H-2**) were improved with a ratio of 1:1000 (M:Al) instead of 1:500. Besides the activities, the late transition metals cobalt and nickel showed very high selectivities towards dimerization products with around 98 % (nickel) and 80 to 93 % (cobalt). In contrast, the product yields with the early transition metal titanium were constantly lower. **C** with a dimer amount of 66 % was the best result of this row. Finally in this section the activities and selectivities raised from titanium over cobalt to nickel.

Table 2. Selectivity towards products and catalytic activity in kg(product) per mol(cat.) per hour. The percentages were determined by relative area integration for each of the oligomers by the carbon atom numbers from the GC.

Catalytic system	C 6 [%]	C 9 [%]	C 12 [%]	C 15 [%]	C 18 [%]	Activity kg/mol/h
A	42	21	18	14	5	23
B	42	23	20	13	1	17
B-2	45	23	19	9	4	20
C	66	21	13	-	-	54
D	80	10	6	4	-	88
E	93	4	3	-	-	134
E-2	91	4	3	2	-	159
F	90	5	3	2	-	50
G	98	2	-	-	-	351
H	98	2	-	-	-	385
H-2	98	1	1	-	-	420
I	99	1	-	-	-	182

7.2.2.2. Homogeneous dimerization reactions with butenes

Having first results with propylene, it was of interest to check higher olefins. Compared to the results of propylene, the dimerization experiments of 1-butene with the nickel catalysts were also very selective of up to 96 % for dimeric products (Table 3). Titanium complexes showed a broader product distribution with 51 – 62 % for dimers and a higher conversion rate of up to 19 %. Surprisingly, cobalt complexes activated with a 1:500 ratio were catalytically inactive (**D**, **E**, **F**). The use of more cocatalyst (**E-2**) made this system active for the dimerization of 1-butene. Nickel complexes were more selective, titanium complexes more active.

Table 3. Selectivity towards products and conversion of 20 ml liquid 1-butene after a reaction time of two hours at 25°C. The percentages were determined by relative area integration for each of the oligomers by the carbon atom numbers from the GC.

	C 8 [%]	C 12 [%]	C 16 [%]	Conversion [%]
A	59	27	14	19
B	60	32	8	15
B-2	51	38	11	16
C	62	27	11	17
D	-	-	-	-
E	-	-	-	-
E-2	40	60	-	2
F	-	-	-	-
G	94	6	-	9
H	96	4	-	11
H-2	89	11	-	11
I	93	7	-	8

The reactions with the internal olefin *cis*-butene showed a remarkable result (Table 4). Only titanium as central metal is active for the dimerization. Low conversion rates but high selectivities reflect the steric difference of an internal olefin. While 1-butene can easily be coordinated and dimerized, *cis*-butene is sterically hindered. Complexes with late transition metals were totally inactive under these reaction conditions.

Table 4. Selectivity towards dimerization reaction products and conversion of 20 ml liquid *cis*-butene after reaction time of two hours at 25°C. The percentages were determined by relative area integration for each of the oligomers by the carbon atom numbers from the GC.

Products	C 8 [%]	Conversion [%]
A	100	0,8
B	100	1,8
B-2	100	2,5
C	100	1,3

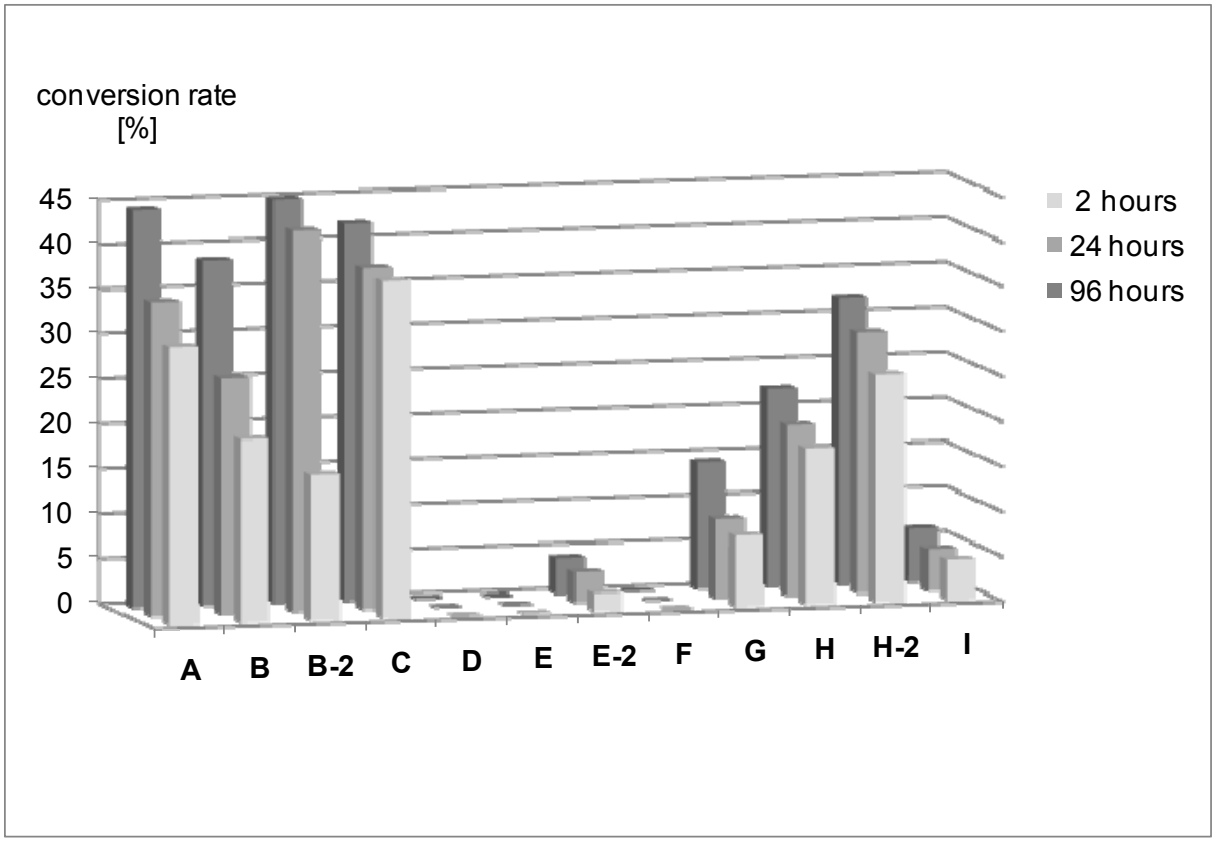
7.2.2.3. Homogeneous dimerization reactions with 1-pentene

Also the 1-pentene dimerization could be attractive. Table 5 shows the results of the dimerization experiments after 2, 24 and 96 hours. Compared to the results of the dimerization of propylene and 1-butene, the dimerization of 1-pentene follows this line. The cobalt containing catalysts were inactive, except with an activation ratio of 1:1000 (M:Al). As seen before, nickel as central metal gives the highest selectivities of up to 100% for dimeric products. Only the catalytic system **G** is slightly less selective than the runs **H**, **H-2** and **I**. Even after a longer reaction time of 96 hours, when more side products can be formed, the selectivity is nearly like the selectivity after two hours. The results with titanium as central metal showed lower selectivities towards dimerization products. With the selectivity after two hours towards C-10 isomers being in the range of 59- 78%, it shrinks to 54- 65% after 96 hours (Table 5, **A**, **B**, **B-2** and **C**). With longer reaction times, more side reactions or further insertion reactions are possible. The dimer can act as an educt olefin and react with the active metal center. There is no dramatic change in the product distribution from 24 to 96 hours. This can lead to the assumption that the system is no longer active after 24 hours. Therefore, it was necessary to take a closer look at the conversion rates.

Table 5. Selectivity towards products of 6 ml 1-pentene after reaction times of 2, 24 and 96 hours at 25°C. The percentages were determined by relative area integration for each of the oligomers by the carbon atom numbers from the GC.

Time	2 h			24 h			96 h		
Carbon number	C 10 [%]	C 15 [%]	C 20 [%]	C 10 [%]	C 15 [%]	C 20 [%]	C 10 [%]	C 15 [%]	C 20 [%]
A	59	33	8	55	33	12	54	36	10
B	71	22	7	67	26	7	60	29	11
B-2	76	18	6	64	27	9	63	28	9
C	78	22	-	61	30	9	60	30	10
D	-	-	-	-	-	-	-	-	-
E	-	-	-	-	-	-	-	-	-
E-2	50	50	-	26	53	21	26	53	21
F	-	-	-	-	-	-	-	-	-
G	85	15	-	83	17	-	82	18	-
H	100	--	-	100	-	-	100	-	-
H-2	100	-	-	99	1	-	95	5	-
I	100	-	-	98	2	-	97	3	-

Scheme 4 clearly shows the conversion rates of the 12 different catalytic systems at three different time periods. The systems **B-2**, **C**, **H**, **H-2** and **I** show no remarkable difference in the conversion rates between 24 and 96 hours. As postulated before, the systems were most active in the first two hours, and the conversion shrank from time to time. Only the experiments **A**, **B** and **G** showed small changes in the conversion between 24 and 96 hours. At this point, for detailed kinetic studies, more experiments have to be performed and more data points need to be discussed.



Scheme 17. Conversion rates products of 6 ml 1-pentene after reaction time of 2, 24 and 96 hours at 25°C. The percentages were determined by relative area integration for each of the oligomers by carbon number from the GC.

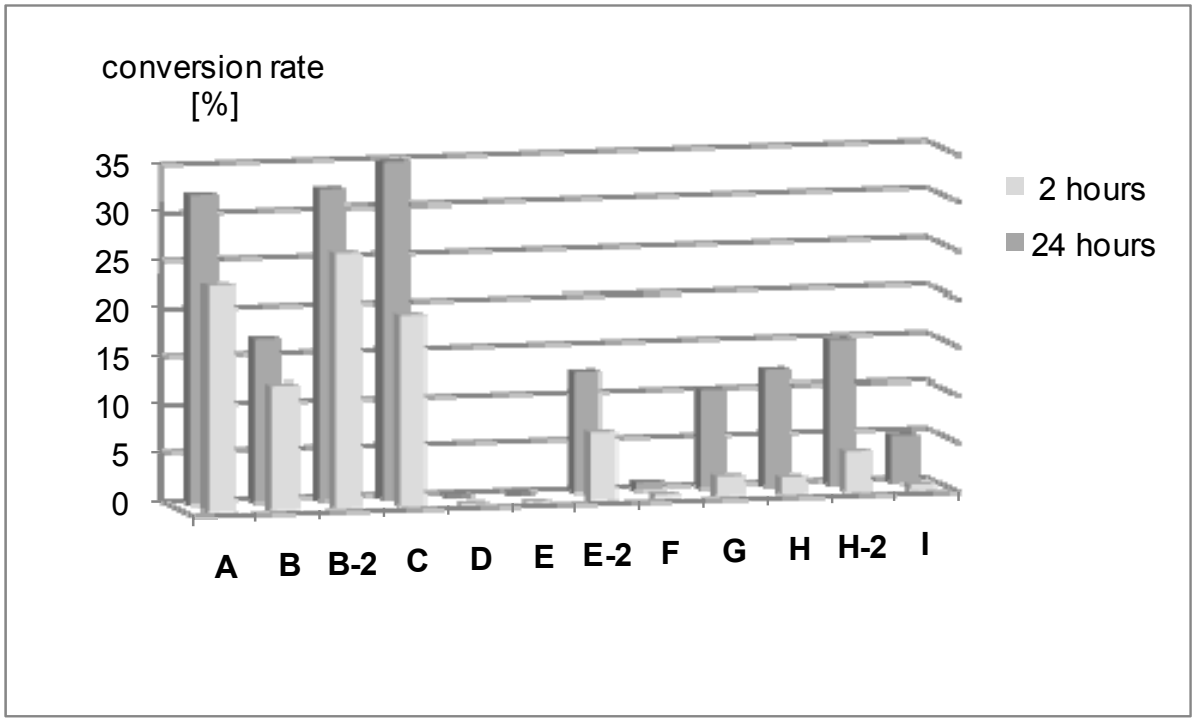
7.2.2.4. Homogeneous dimerization reactions with 1-hexene

As expected, the dimerization of 1-hexene mirrors the results from the experiments with 1-pentene. All three metals in these complexes show the typical behavior as seen before (Table 6). Nickel catalysts are very selective of up to 100 % for dimeric products. **G** is again slightly lower selective than the other experiments with nickel complexes, except **H-2** after two hours. The titanium system produces dimers, trimers and tetramers. It is less selective but shows higher conversion rates than the nickel system (Scheme 5). While nickel and titanium complexes are active in the catalytic dimerization, cobalt as central metal is only active after activation with MAO in a ratio of 1:1000 (M:Al).

Table 6. Selectivity towards products of 6 ml 1-hexene after reaction time of 2, 24 and 96 hours at 25°C. The percentages were determined by relative area integration for each of the oligomers by the carbon atom numbers from the GC.

Reaction time	2 h			24 h		
Carbon number	C 12 [%]	C 18 [%]	C 24 [%]	C 12 [%]	C 18 [%]	C 24 [%]
A	82	18	-	80	18	2
B	89	11	-	78	22	-
B-2	69	24	7	63	28	10
C	85	15	-	80	20	-
D	-	-	-	-	-	-
E	-	-	-	-	-	-
E-2	53	40	7	29	46	25
F	-	-	-	-	-	-
G	90	10	-	83	17	-
H	100	-	-	100	-	-
H-2	89	7	4	84	10	6
I	100	-	-	85	15	-

Scheme 5 shows that titanium is the most active metal center for the dimerization of 1-hexene. Raising the activation ratio has a positive effect on the conversion ratio as seen in experiments **B** and **B-2**, **E** and **E-2** and **H** and **H-2**. An elongation of the reaction time from two up to 24 hours can lift the conversion rates drastically (**A**, **C**, **G**, **H**, **H-2** and **I**) or slightly (**B**, **B-2** and **E-2**). Compared to the dimerization of 1-pentene, the conversion rates are lower (from 45% down to 35%).



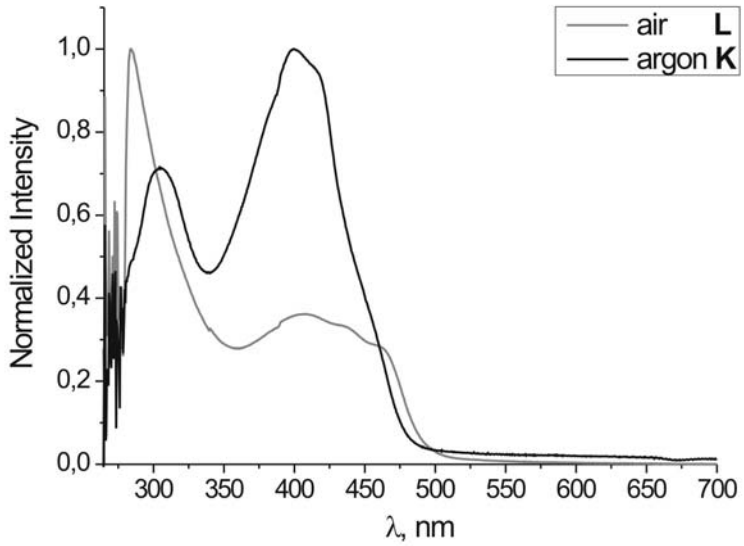
Scheme 18. Conversion rates products of 6 ml 1-hexene after reaction time of 2, 24 and 96 hours at 25°C. The percentages were determined by relative area integration for each of the oligomers by the carbon atom numbers from the GC.

7.2.2.5. Fluorescent properties

We call it a smart catalytic system, because the system gives alert when it gets deactivated or polluted. The system turns from yellow to lime green after exposition to the surrounding air and the system becomes catalytically inactive. In the following section, we investigated the luminescent and fluorescent properties of the system under **argon** (**K**) and **air** (**L**). The composition **A** was taken and divided in two portions after the activation time of 30 minutes. Sample **K** was stirred under argon, sample **L** was treated with air for 30 minutes.

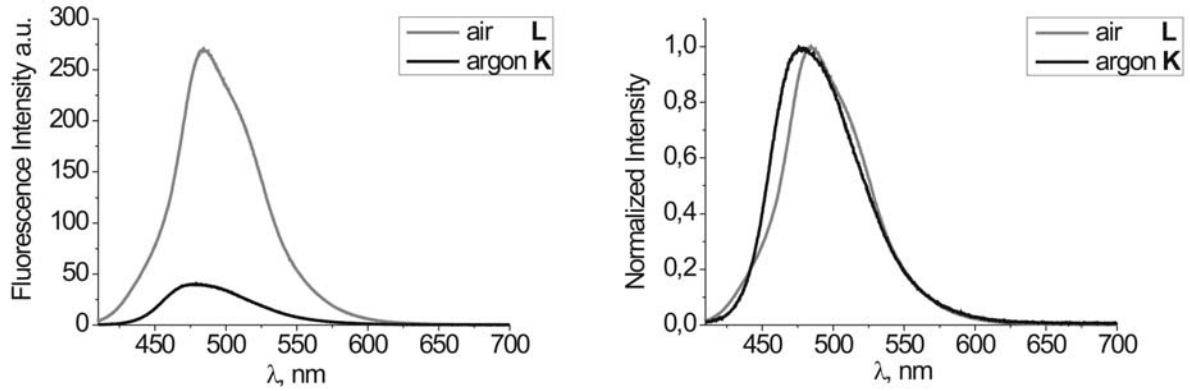
UV-vis data provide information on the possibility of the absorption transition between the ground and excited states of the molecules. Both catalytic systems have two major absorption bands. Scheme 6 exhibits UV-vis spectra of **K** and **L** in toluene. **K** has its absorption maximum at 400 nm, whereas **L** shows a local absorption maximum. On the other side, the absorption maximum after opening the system is shifted to 284 nm, while **K** shows a side peak. It is obvious that both systems illustrate different absorption spectra with different maxima. To open the system and

to expose it to normal air, seems to have a great influence on the composition and the luminescent properties of the catalytic system.



Scheme 19. Normalized absorption spectra before and after opening of the system, in the range of 260-700 nm.

Scheme 7 shows very markable the dissimilar behavior of the fluorescence measurements. The samples were excitated at 400 nm. The fluorescence intensity of **L** is seven times higher (although 400 nm is just a local maximum for **L**) than the fluorescence of **K** with the same concentration. Besides the intensity, the shapes of the fluorescent spectra are different. The right side of Scheme 7 illustrates the normalized (divided by maximum) spectra of both **K** and **L**. The maximum of the graph of **K** (479) is shifted to lower wavelengths compared to **L** (484). Even the shape is different; **L** shows a small shoulder between 510 and 520 nm. This and the results of the absorption measurements explain the different color of the two samples.



Scheme 20. Fluorescence spectra with excitation at 400nm. Intensity dependent and normalized spectra of K and L.

7.3. Summary and conclusion

In summary, we report a highly selective system for the dimerization of olefins. The activities of the catalytic dimerizations shrank with the number of carbons of the olefins. The shorter the olefin the higher the activity. Not only the kind of olefin has an effect on the dimerization results but also the metal center of the corresponding complexes. While nickel showed the best results for propylene, titanium was most active for 1-pentene and 1-hexene. Cobalt was not as catalytic active as the other central metals. It was very important to observe the activation ratio. A change from 1:500 to 1:1000 raised the activity in all cases. Some experiments showed only activity with this higher activation ratio. Obviously the amount of active centers is depended on the concentration of the cocatalyst. In all experiments with different olefins, nickel complexes showed excellent selectivities towards dimeric products. In most cases 100% were observed. Titanium and cobalt containing complexes reached well to high dimer yields but were in all cases lower than nickel. For all the runs, no high molecular weight products were observed.

The system showed a smart behavior. The color turned from yellow to lime green after exposition to the surrounding air. With this color change, the system gets catalytically inactive; it gives alert when it gets deactivated or polluted.

7.4. Experimental Section

7.4.1. General considerations

Air- and moisture sensitive reactions were carried out under an atmosphere of purified argon using conventional Schlenk or glove box techniques. The dimerization reactions were performed with pressure Schlenk tubes.

The products of the dimerization experiments were characterized by a gas chromatograph (Agilent 6890) and GC/MS (FOCUS DSQ^{TM} Thermo Scientific). NMR spectra were taken on a Varian Inova 400 instrument. The samples were prepared under argon atmosphere and measured at room temperature. Chemical shifts (δ, ppm) were recorded relative to the residual solvent peak at δ = 7.24 ppm for chloroform-*d*. The multiplicities were assigned as follows: s, singlet; m, multiplet; t, triplet. ^{13}C {^{1}H} NMR spectra were fully proton decoupled and the chemical shifts (δ, ppm) are relative to the solvent peak (77.0 ppm).

UV-vis spectra were taken on a U-3310 Spectrophotometer. Instrument Parameters: Measurement Type: Wavelength Scan, Data Mode: Abs, Starting Wavelength: 700.00 nm, Ending Wavelength: 250.00 nm, Scan Speed: 300 nm/min, Sampling Interval: 0.50 nm, Slit Width: 4 nm, PMT Voltage: Auto, Lamp Change: 340.00 nm, Path Length: 10.0 mm

The excitation for fluorescence spectroscopy was 400.00 nm.

7.4.2. Materials

All solvents were purchased as technical grade and purified by distillation over Na/K alloy under an argon atmosphere. All other chemicals were purchased commercially from Aldrich or Acros or were synthesized according to literature procedures. The methyl aluminoxane solution (MAO, 10 wt.% in toluene) was obtained from Albemarle, USA.

7.4.3 Dimerization reactions with propylene and 1-butene and cis-butene

The respective metal salts were combined with the organic compound **L** in different ratios and activated with MAO solution. The respective metal salt (6 µmol) and ligand

precursor **L** were combined and stirred until a color change occurred (ca. 1h) and transferred into a 400 ml pressure Schlenk tube. The cocatalyst (MAO solution) was added and stirred for 30 min. Then the dimerization experiments were started. The pressure Schlenk tube was filled with 50 ml liquid propylene and closed, warmed to room temperature with an external water bath and stirred. After the reaction time of 1 hour, the Schlenk tube was opened and the solution was analyzed by GC. Cyclooctane was used as standard. Samples were taken at -10°C.
In the case of 1-butene and *cis*-butene, an amount of 20 ml liquid olefin was filled into the pressure Schlenk tube. The olefin was warmed to room temperature and the reaction vessel was opened after a reaction time of 2 hours. The percentages of the products were determined by relative area integration for each of the oligomers by carbon atom numbers from the GC, with cyclooctane as internal standard.

7.4.4 Dimerization reactions with 1-pentene and 1-hexene

The experiments were performed according to *6.4.3,* but in normal Schlenk tubes. 6 ml liquid olefin was added after activation. Samples were taken as reported.

7.5. Acknowledgement

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7.6. References

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8. List of Publications

1. 1,2-,1,7- and 1,12-dicarba-closo-dodecaborane(12) derivates revisited by 13C NMR spectroscopy and DFT calculations. First observation of isotope-induced chemical shifts 1Δ10/11B(13C), and the signs and magnitudes of coupling constants 1J(13C,13C)and 1J(13C,11B)
   B. Wrackmeyer, Z. G. Hernandez, J. Lang, O. L. Tok; ZAAC 2009, *635,* 1087-1093.

The following publications have been published, are submitted or are to be submitted during the work on this thesis:

2. Homogeneous catalytic dimerization of propylene with bis(imino)pyridine vanadium(III) complexes
   J. R. V. Lang, C. E. Denner, H. G. Alt; J. Mol. Cat. A: Chemical 322 (2010) 45-49.

3. Highly active dimerization of olefins using nickel phosphine catalysts
   J. R. V. Lang, H. G. Alt; submitted, J. Mol. Cat. A: Chemical July (2010).

4. Practical heterogeneous complexes and their application as magnetically separable olefin dimerization catalysts
   J. R. V. Lang, H. G. Alt; to be submitted.

5. A smart catalytic system for the dimerization of olefins
   J. R. V. Lang, J. Ewert, H. G. Alt; to be submitted.

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10. Erklärung

Hiermit erkläre ich, dass ich die Arbeit selbständig verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt habe.

Ferner habe ich nicht versucht, anderweitig mit oder ohne Erfolg eine Dissertation einzureichen oder mich der Doktorprüfung zu unterziehen.

Bayreuth, 21.10.10 Julian Lang